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(54) Title: SHADING COMPOSITION

(57) Abstract: The present invention relates to a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, which produces in the CIElab colour coordinate system a relative hue angle of 220-320°, to a detergent composition, a fabric softener composition as well as to a shading

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Shading composition

The present invention relates to a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, which produces in the CIElab colour coordinate system a relative hue angle of $220 - 320^\circ$, to a detergent
5 composition, to a fabric softener composition as well as to a shading process using such a mixture.

A frequently employed method in bleaching and whitening is to use violet or blue dyes concurrently in order to improve the bleaching and whitening effect. If such a dye is used in conjunction with a fluorescent whitening agent, this can serve two different purposes. On the
10 one hand, it is possible to try to achieve an increase in the degree of whiteness by compensating for the yellow of the fabric, in which case the white shade produced by the fluorescent whitening agent on the fabric is largely retained. On the other hand, the object can be to effect with the dye in question a change in the shade of the white effect produced by the fluorescent whitening agent on the fabric, in which case too an attempt is made
15 additionally to achieve an increase in the degree of whiteness. It is thus possible to adjust the desired shade of the white effect.

Shading processes of materials such as paper and textile fabrics are known from e.g. DE 3125495.

20 These disclosed shading processes, respectively the disclosed mixtures of photocatalyst and dyestuff are not suitable for a regular use, such as in detergent or softener formulations, because the dyestuffs do accumulate with every use and after a few uses the fabrics are coloured.

Therefore, the goal of the present invention was to find a mixture of at least one
25 photocatalyst and at least one azo and/or triphenylmethane dyestuff, which does not lead to a colouration of the fabric.

This problem was solved by a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, which produces a relative hue angle of $220 - 320^\circ$, which is not light stable. That means that the components of the
30 mixture, when applied to the fabric are destroyed by light.

Surprisingly, when the dyestuff as such (without the photocatalyst) is applied to the fabric, it is not destroyed (or destroyed much slower).

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Therefore the present invention relates to a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, which produce a relative hue angle of $220 - 320^\circ$ and wherein the dyestuff component is degraded when the composition is exposed to light.

- 5 Colour coordinates and colour differences are expressed using the internationally standardized CIELAB tristimulus values:

a^* = red – green (+, –)

b^* = yellow – blue (+, –)

L^* = lightness (light = 100)

- 10 C^* = chroma

H^* = hue (angle of 0° = red, 90° = yellow, 180° = green, 270° = blue),

and the colour differences ΔE^* , ΔH^* , ΔC^* , ΔL^* , Δa^* , and Δb^* , together with an identification number of the sample.

- This internationally accepted system has been developed by CIE ("Commission
15 Internationale de l'Éclairage"). It is for example part of DIN 6174: 1979-01 as well as DIN 5033-3: 1992-07.

- Preferably the present invention relates to a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff,
20 which produce a relative hue angle of $220 - 320^\circ$ and wherein the dyestuff component is degraded when the composition is exposed to sunlight.

- More preferably the present invention relates to a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff,
25 which produce a relative hue angle of $220 - 320^\circ$ and wherein the decrease rate of the azo dyestuff(s) and/or the triphenylmethane dyestuff(s) is at least 1 % per 2 hours, preferably at least 2 % when the composition is exposed to sunlight.

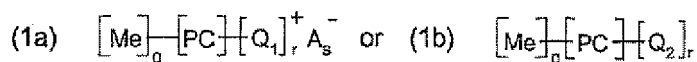
- The degradation of the components can be determined spectrophotometrically.
30

Preferably, the photocatalyst is a phthalocyanine.

More preferably, the photocatalyst is a water-soluble phthalocyanine of Zn, Fe(II), Ca, Mg, Na, K, Al, Si(IV), P(V), Ti(IV), Ge(IV), Cr(VI), Ga(III), Zr(IV), In(III), Sn(IV) or Hf(VI);

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Most preferably, the photocatalyst is a water-soluble phthalocyanine of the formula



in which

PC is the phthalocyanine ring system;

5 Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Zr; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

Z₁ is a halide; sulfate; nitrate; carboxylate; alkanolate; or hydroxyl ion;

q is 0; 1 or 2;

r is 1 to 4;

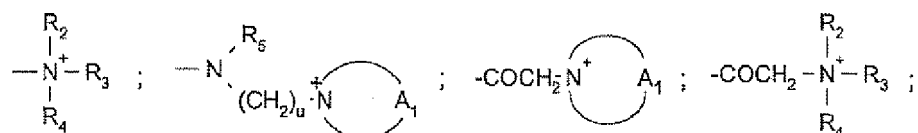
10 Q₁ is a sulfo or carboxyl group; or a radical of the formula
 $-\text{SO}_2\text{X}_2-\text{R}_1-\text{X}_3^+$; $-\text{O}-\text{R}_1-\text{X}_3^+$; or $-(\text{CH}_2)_t-\text{Y}_1^+$;

in which

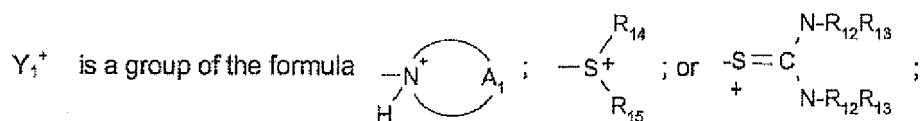
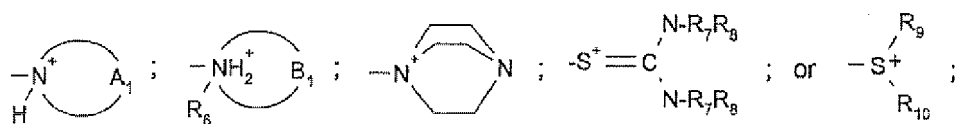
R₁ is a branched or unbranched C₁-C₈alkylene; or 1,3- or 1,4-phenylene;

X₂ is -NH-; or -N-C₁-C₅alkyl;

15 X₃⁺ is a group of the formula



or, in the case where R₁ = C₁-C₈alkylene, also a group of the formula



20 t is 0 or 1;

where in the above formulae

R₂ and R₃ independently of one another are C₁-C₆alkyl;

R₄ is C₁-C₆alkyl; C₅-C₇cycloalkyl or NR₇R₈;

R₅ and R₆ independently of one another are C₁-C₅alkyl;

25 R₇ and R₈ independently of one another are hydrogen or C₁-C₅alkyl;

- 4 -

R_9 and R_{10} independently of one another are unsubstituted C_1 - C_6 alkyl or C_1 - C_6 alkyl substituted by hydroxyl, cyano, carboxyl, carb- C_1 - C_6 alkoxy, C_1 - C_6 alkoxy, phenyl, naphthyl or pyridyl;

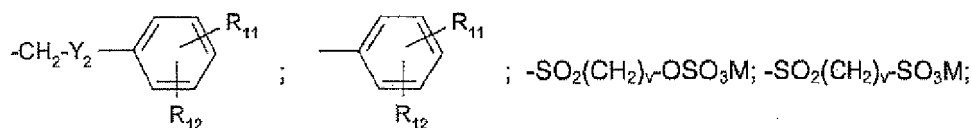
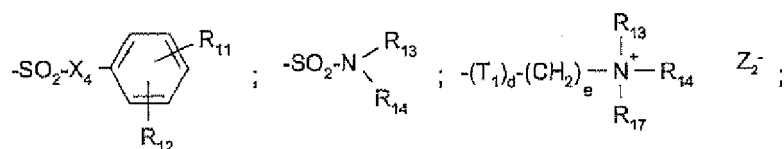
u is from 1 to 6;

5 A_1 is a unit which completes an aromatic 5- to 7-membered nitrogen heterocycle, which may where appropriate also contain one or two further nitrogen atoms as ring members, and

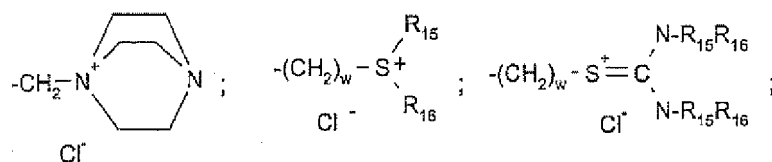
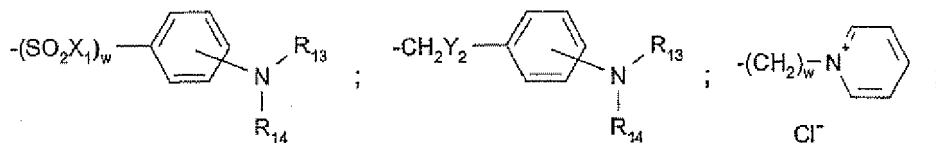
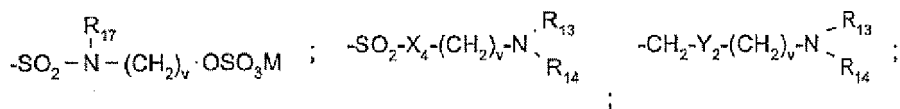
B_1 is a unit which completes a saturated 5- to 7-membered nitrogen heterocycle, which may where appropriate also contain 1 to 2 nitrogen, oxygen and/or sulfur atoms as ring members;

10

Q_2 is hydroxyl; C_1 - C_{22} alkyl; branched C_3 - C_{22} alkyl; C_2 - C_{22} alkenyl; branched C_3 - C_{22} alkenyl and mixtures thereof; C_1 - C_{22} alkoxy; a sulfo or carboxyl radical; a radical of the formula



15



- 5 -

a branched alkoxy radical of the formula
$$\begin{array}{c} \text{CH}_2-(\text{O})_a(\text{CH}_2)_b(\text{OCH}_2\text{CH}_2)_c-\text{B}_2 \\ | \\ -\text{O}-\text{CH} \\ | \\ \text{CH}_2-(\text{O})_a(\text{CH}_2)_b(\text{OCH}_2\text{CH}_2)_c-\text{B}_2 \end{array};$$

$$\begin{array}{c} -\text{O}-\text{CH}_2 \\ | \\ \text{CH}-(\text{O})_a(\text{CH}_2)_b(\text{OCH}_2\text{CH}_2)_c-\text{B}_2 \\ | \\ \text{CH}_2-(\text{O})_a(\text{CH}_2)_b(\text{OCH}_2\text{CH}_2)_c-\text{B}_2 \end{array};$$
 an alkylethyleneoxy unit of the formula

$-(\text{T}_1)_d-(\text{CH}_2)_b(\text{OCH}_2\text{CH}_2)_a-\text{B}_3$ or an ester of the formula COOR_{18}

in which

- 5 B_2 is hydrogen; hydroxyl; $\text{C}_1\text{-C}_{30}$ alkyl; $\text{C}_1\text{-C}_{30}$ alkoxy; $-\text{CO}_2\text{H}$; $-\text{CH}_2\text{COOH}$; $-\text{SO}_3^-\text{M}_1$; $-\text{OSO}_3^-\text{M}_1$; $-\text{PO}_3^{2-}\text{M}_1$; $-\text{OPO}_3^{2-}\text{M}_1$; and mixtures thereof;
- B_3 is hydrogen; hydroxyl; $-\text{COOH}$; $-\text{SO}_3^-\text{M}_1$; $-\text{OSO}_3^-\text{M}_1$ or $\text{C}_1\text{-C}_6$ alkoxy;
- M_1 is a water-soluble cation;
- T_1 is $-\text{O}-$; or $-\text{NH}-$;
- 10 X_1 and X_4 independently of one another are $-\text{O}-$; $-\text{NH}-$ or $-\text{N-C}_1\text{-C}_6$ alkyl;
- R_{11} and R_{12} independently of one another are hydrogen; a sulfo group and salts thereof; a carboxyl group and salts thereof or a hydroxyl group; at least one of the radicals R_{11} and R_{12} being a sulfo or carboxyl group or salts thereof,
- Y_2 is $-\text{O}-$; $-\text{S}-$; $-\text{NH}-$ or $-\text{N-C}_1\text{-C}_6$ alkyl;
- 15 R_{13} and R_{14} independently of one another are hydrogen; $\text{C}_1\text{-C}_6$ alkyl; hydroxy- $\text{C}_1\text{-C}_6$ alkyl; cyano- $\text{C}_1\text{-C}_6$ alkyl; sulfo- $\text{C}_1\text{-C}_6$ alkyl; carboxy or halogen- $\text{C}_1\text{-C}_6$ alkyl; unsubstituted phenyl or phenyl substituted by halogen, $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy; sulfo or carboxyl or R_{13} and R_{14} together with the nitrogen atom to which they are bonded form a saturated 5- or 6-membered heterocyclic ring which may additionally also contain a nitrogen or
- 20 oxygen atom as a ring member;
- R_{15} and R_{16} independently of one another are $\text{C}_1\text{-C}_6$ alkyl or aryl- $\text{C}_1\text{-C}_6$ alkyl radicals;
- R_{17} is hydrogen; an unsubstituted $\text{C}_1\text{-C}_6$ alkyl or $\text{C}_1\text{-C}_6$ alkyl substituted by halogen, hydroxyl, cyano, phenyl, carboxyl, carb- $\text{C}_1\text{-C}_6$ alkoxy or $\text{C}_1\text{-C}_6$ alkoxy;
- R_{18} is $\text{C}_1\text{-C}_{22}$ alkyl; branched $\text{C}_3\text{-C}_{22}$ alkyl; $\text{C}_1\text{-C}_{22}$ alkenyl or branched $\text{C}_3\text{-C}_{22}$ alkenyl;
- 25 $\text{C}_3\text{-C}_{22}$ glycol; $\text{C}_1\text{-C}_{22}$ alkoxy; branched $\text{C}_3\text{-C}_{22}$ alkoxy; and mixtures thereof;
- M is hydrogen; or an alkali metal ion or ammonium ion,
- Z_2^- is a chlorine; bromine; alkylsulfate or aralkylsulfate ion;
- a is 0 or 1;
- b is from 0 to 6;

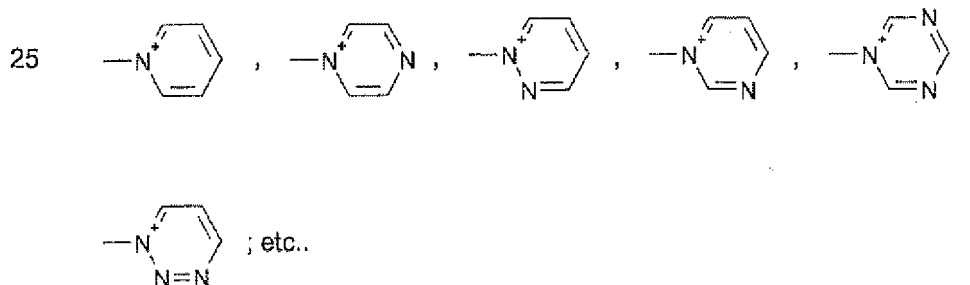
- 6 -

- c is from 0 to 100;
 d is 0; or 1;
 e is from 0 to 22;
 v is an integer from 2 to 12;
 5 w is 0 or 1; and
 A⁻ is an organic or inorganic anion, and
 s is equal to r in cases of monovalent anions A⁻ and is ≤ r in cases of polyvalent anions, it being necessary for A_s⁻ to compensate the positive charge; where, when r ≠ 1, the radicals Q_i can be identical or different,
 10 and where the phthalocyanine ring system may also comprise further solubilising groups.

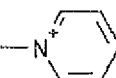
The number of substituents Q₁ and Q₂ in the formula (1a) and (1b) respectively, which may be identical or different, is between 1 and 8, and it is not imperative, as is generally the case with phthalocyanines, for it to be an integer (degree of substitution). If other noncationic
 15 substituents are present, the sum of the latter and the cationic substituents is between 1 and 4. The minimum number of substituents which must be present in the molecule is governed by the solubility of the resulting molecule in water. It is sufficiently soluble in water when enough of the phthalocyanine compound dissolves to effect a photodynamically catalysed oxidation on the fibre. A solubility as low as 0.01 mg/l may suffice, although one of from
 20 0.001 to 1 g/l is generally advantageous.

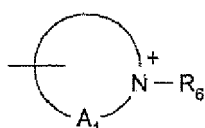
Halogen means fluorine, bromine or, in particular, chlorine.

Especially suitable groups  are:



- 7 -

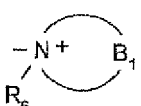
Preference is given to the group  ;

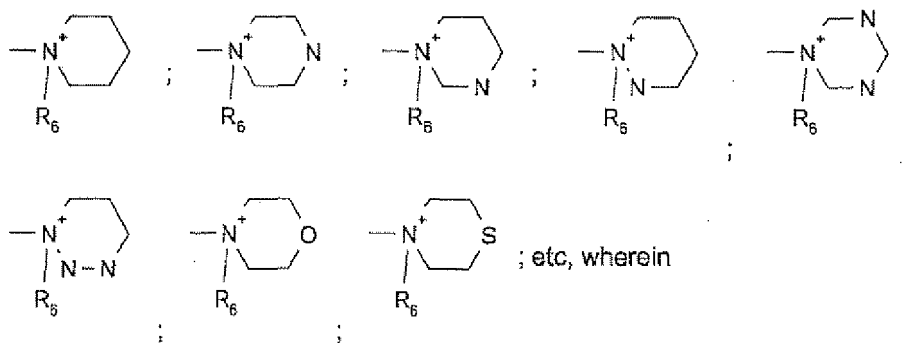
Suitable heterocyclic rings in the group  are likewise the groups listed

above, the bond to the other substituents merely being via a carbon atom.

- 5 In all of these substituents, phenyl, naphthyl and aromatic hetero rings may be substituted by one or two further radicals, for example by C₁-C₆alkyl, C₁-C₆alkoxy, halogen, carboxyl, carb-C₁-C₆alkoxy, hydroxyl, amino, cyano, sulfo, sulfonamido, etc.

- 10 Preference is given to a substituent from the group C₁-C₆alkyl, C₁-C₆alkoxy, halogen, carboxyl, carb-C₁-C₆alkoxy or hydroxyl.

Particularly suitable groups  are:



B₁ and R₆ have the same meaning as defined above.

15

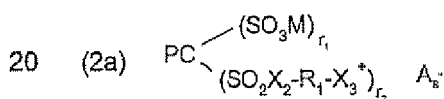
All of the aforementioned nitrogen heterocycles can also be substituted by alkyl groups, either on a carbon atom or on another nitrogen atom in the ring. The alkyl group is preferably the methyl group.

- 20 A_s in formula (1a) is, as a counterion to the positive charge on the remainder of the molecule, any anion. In general, it is introduced by the preparation process (quaternization).

- 8 -

- It is then preferably a halogen ion, an alkylsulfate or an arylsulfate ion. Arylsulfate ions which may be mentioned are the phenylsulfonate, p-tolylsulfonate and the p-chlorophenylsulfonate ion. The anion can however also be any other anion since the anions can be readily exchanged in a known manner; A_s^- can thus also be a sulfate, sulfite, carbonate, phosphate, nitrate, acetate, oxalate, citrate, lactate ion or another anion of an organic carboxylic acid.
- The index s is the same as r for monovalent anions. For polyvalent anions, s has a value $\leq r$, in which case it must be chosen, depending on the conditions, such that it exactly balances the positive charge on the remainder of the molecule.
- 5 C_1 - C_6 alkyl and C_1 - C_6 alkoxy are straight-chain or branched alkyl or alkoxy radicals, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl, tert-amyl or hexyl or methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy, tert-amyloxy or hexyloxy.
- 10 C_2 - C_{22} alkenyl is, for example, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, iso-dodecenyl, n-dodec-2-enyl or n-octadec-4-enyl.

Preferred photobleaching agents of the formula (1a) have the formula



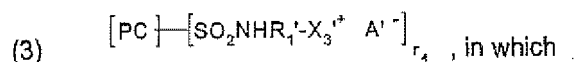
in which

PC, X_2 , X_3 , and R_1 are as defined above;

M is hydrogen; an alkali metal ion; ammonium ion or amine salt ion;

and the sum of the numbers r_1 and r_2 is from 1 to 4 and

- 25 A_s^- balances exactly the positive charge on the remainder of the molecule, and in particular the formula

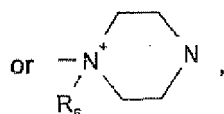
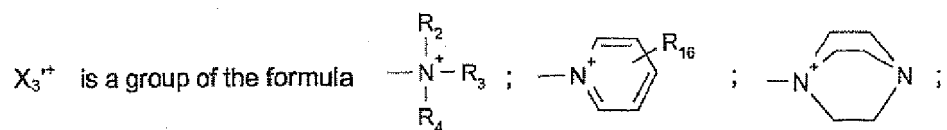


PC is as defined in formula (1a),

R_1' is C_2 - C_8 alkylene;

- 30 r_1 is a number from 1 to 4;

- 9 -



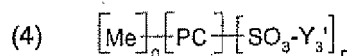
in which

 R_2 and R_3 independently of one another are unsubstituted C_1 - C_4 alkyl or C_1 - C_4 alkyl

5 substituted by hydroxyl, cyano, halogen or phenyl;

 R_4 is R_2 ; cyclohexyl or amino; R_6 is C_1 - C_4 alkyl; R_{16} is C_1 - C_4 alkyl; C_1 - C_4 alkoxy; halogen; carboxyl; carb- C_1 - C_4 alkoxy or hydroxyl; and A^- is a halide; alkylsulfate or arylsulfate ion;10 it being possible for the radicals $-\text{SO}_2\text{NHR}'_1-X_3^{+}A^-$ to be identical or different.

Other photobleaching agents which can be used according to the invention have the formula

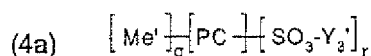


in which

15 PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al- Z_1 ; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV);
In(III); Sn(IV) or Hf(VI); Z_1 is a halide; sulfate; nitrate; carboxylate; alkanolate; or hydroxyl ion; q is 0; 1; or 2;20 Y_3' is hydrogen; an alkali metal ion or ammonium ion; and r is any number from 1 to 4.

Very particularly preferred phthalocyanine compounds have the formula (4a),



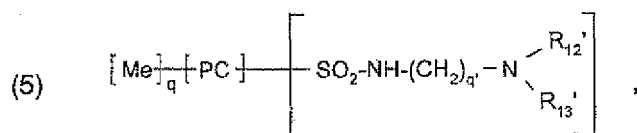
25 in which

Me is Zn or Al- Z_1 ;

- 10 -

- Z_1 is a halide; sulfate; nitrate; carboxylate; alkanolate; or hydroxyl ion,
 PC is the phthalocyanine ring system,
 q is 0; 1; or 2;
 Y_3' is hydrogen; an alkali metal ion or ammonium ion; and
 5 r is any number from 1 to 4.

Other interesting phthalocyanine compounds which can be used according to the invention have the formula



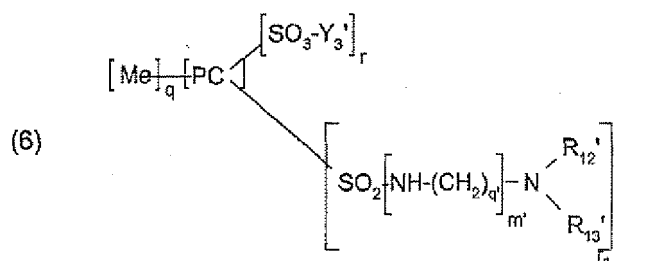
- 10 in which
 PC , Me and q are as defined in formula (4);
 R_{12}' and R_{13}' independently of one another are hydrogen; phenyl; sulfophenyl;
 carboxyphenyl; C_1 - C_8 alkyl; hydroxy- C_1 - C_6 alkyl; cyano- C_1 - C_6 alkyl; sulfo- C_1 - C_6 alkyl;
 carboxy- C_1 - C_6 alkyl or halogen- C_1 - C_6 alkyl or R_{12}' and R_{13}' together with the nitrogen
 15 atom form the morpholine ring;
 q' is an integer from 2 to 6; and
 r is a number from 1 to 4;

where, if $r > 1$, the radicals $-SO_2-NH-(CH_2)_{q'}-N \begin{array}{l} R_{12}' \\ R_{13}' \end{array}$

present in the molecule may be identical or different.

- 20 Further interesting phthalocyanine compounds which can be used according to the invention have the formula

- 11 -



in which

PC, Me and q are as defined in formula (4),

Y₃⁺ is hydrogen; an alkali metal ion or ammonium ion,

5 q' is an integer from 2 to 6;

R₁₂' and R₁₃' independently of one another are hydrogen; phenyl; sulfophenyl;carboxyphenyl; C₁-C₆alkyl; hydroxy-C₁-C₆alkyl; cyano-C₁-C₆alkyl; sulfo-C₁-C₆alkyl;carboxy-C₁-C₆alkyl or halogen-C₁-C₆alkyl or R₁₂' and R₁₃' together with the nitrogen

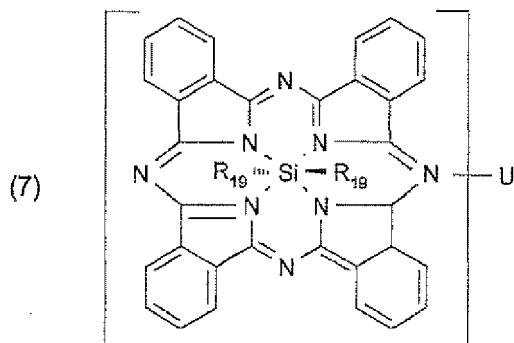
atom form the morpholine ring;

10 m' is 0 or 1; and

r and r₁ independently of one another are any number from 0.5 to 3, the sum r + r₁ being at least 1, but no more than 4.

If the central atom Me in the phthalocyanine ring is Si(IV), the phthalocyanines used

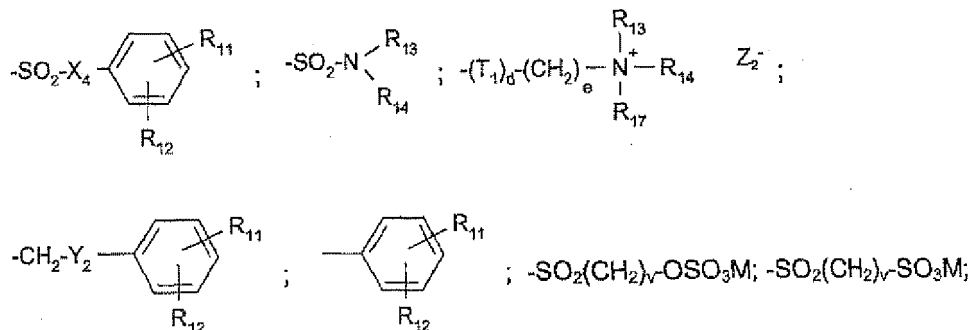
15 according to the invention may also have axial substituents (= R₁₉) in addition to the substituents on the phenyl ring of the phthalocyanine ring. Such phthalocyanines have, for example, the formula



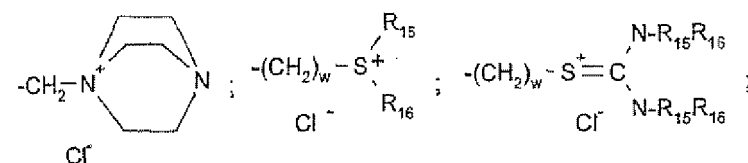
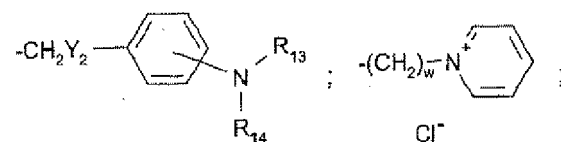
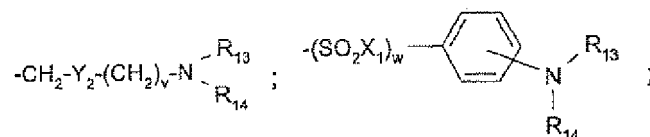
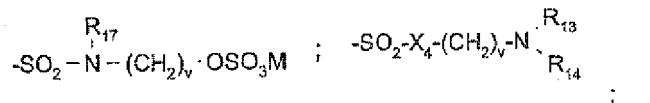
in which

- 12 -

R_{19} is hydroxyl; C_1 - C_{22} alkyl; branched C_3 - C_{22} alkyl; C_1 - C_{22} alkenyl; branched C_3 - C_{22} alkenyl and mixtures thereof; C_1 - C_{22} alkoxy; a sulfo or carboxyl radical; a radical of the formula

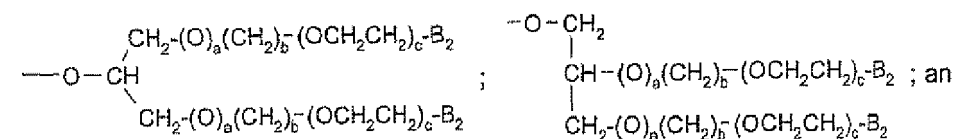


5



10

a branched alkoxy radical of the formula



alkylethyleneoxy unit of the formula $-(T_1)_d-(CH_2)_b(OCH_2CH_2)_a-B_3$ or an ester of the formula $COOR_{18}$; and

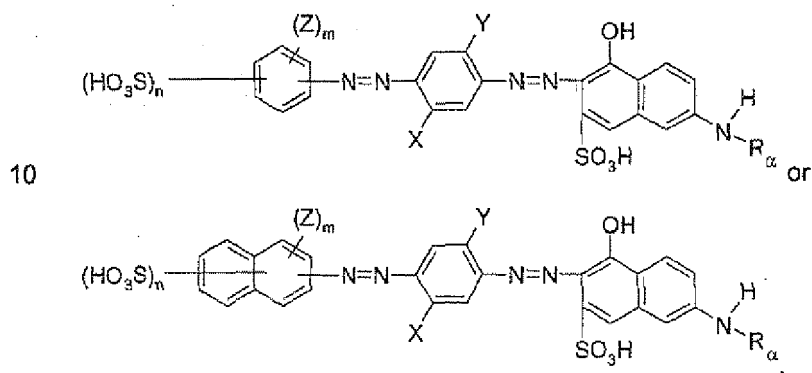
- 13 -

U is $[Q_1]_r^+A_s^-$ or Q_2 , wherein

R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , R_{17} , R_{18} , B_2 , B_3 , M , Q_1 , Q_2 , A^- , T_1 , X_1 , X_4 , Y_2 , Z_2^- , a , b , c , d , e , r , s , v , w are as defined in the formulae (1a) and (1b).

- 5 Especially preferred phthalocyanine compounds are such compounds which are commercially available and used in washing agent compositions. Usually, the anionic phthalocyanine compounds are in the form of alkali metal salts, especially sodium salts.

Suitable azo dyes are for example such as described in US 5211719 of formulae



wherein

X and Y, independently of one another, are each hydrogen; C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy,

R_α is hydrogen or aryl,

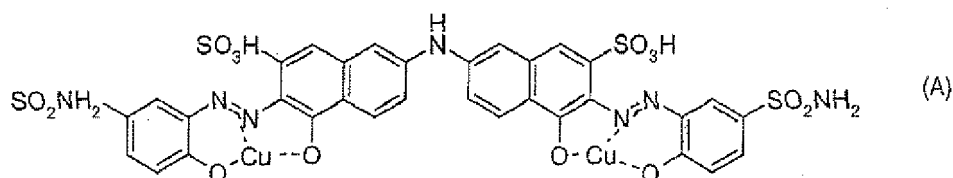
- 15 Z is C_1 - C_4 -alkyl; C_1 - C_4 -alkoxy; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

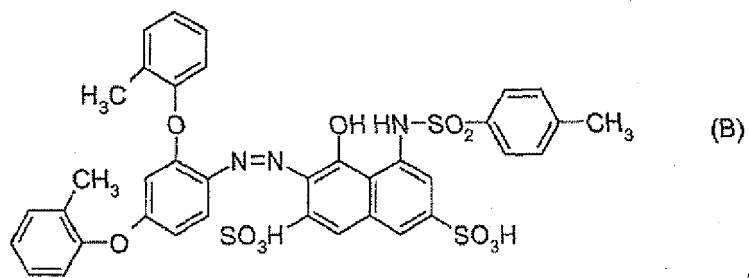
m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof.

Preferably, the azo dyestuffs are compounds of the following formulae

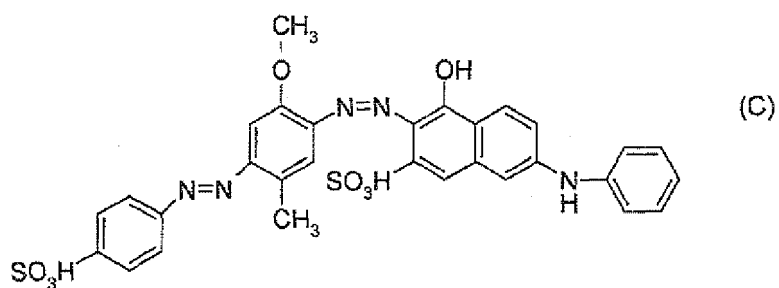
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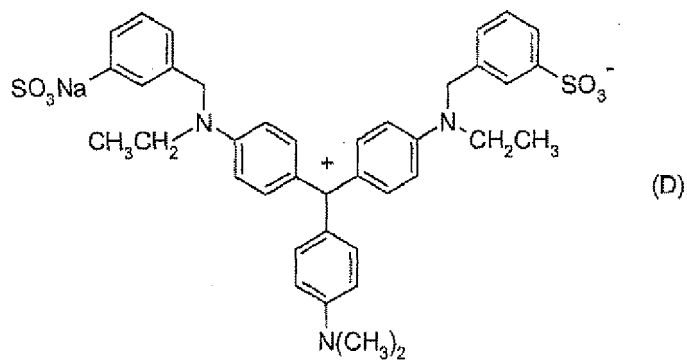
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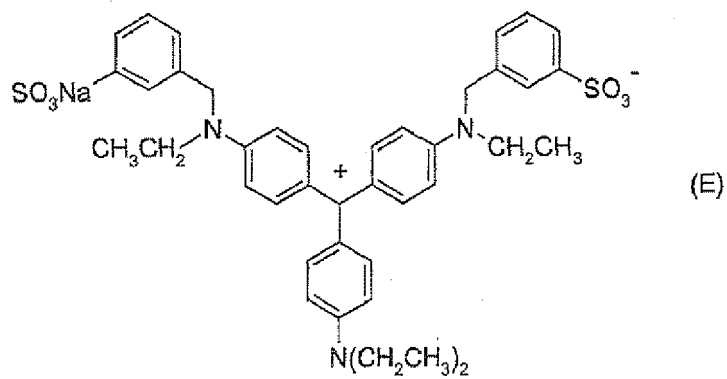
and



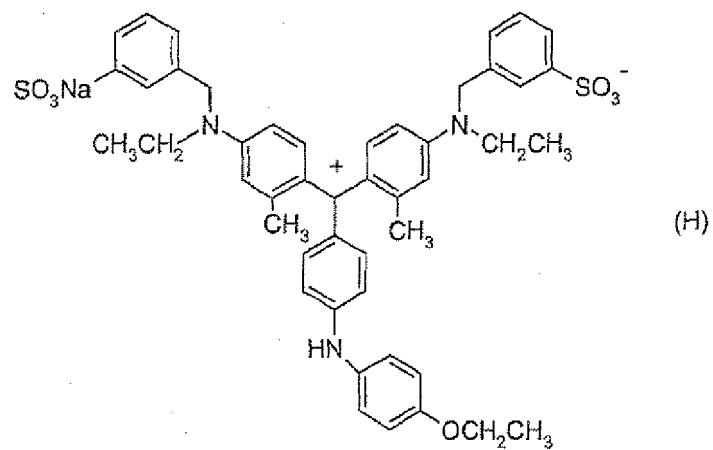
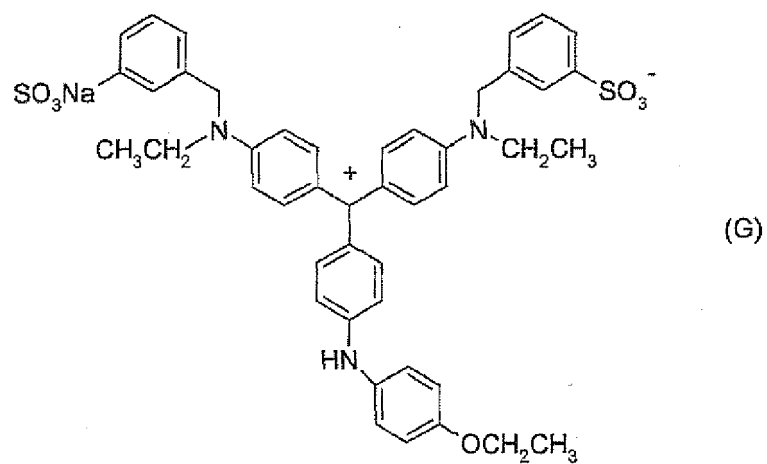
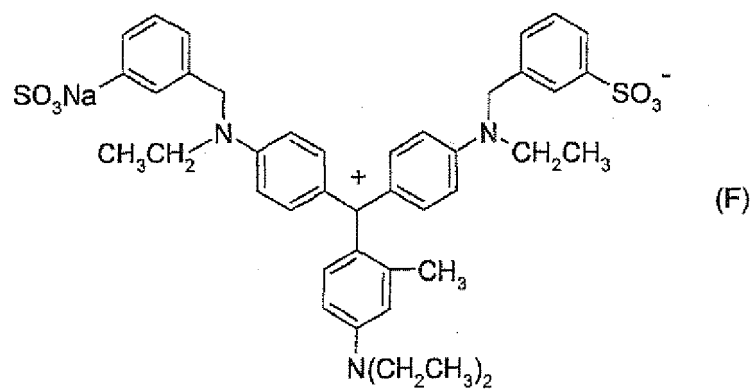
Preferably, the triphenylmethane dyestuffs are compounds of the following formulae:



5

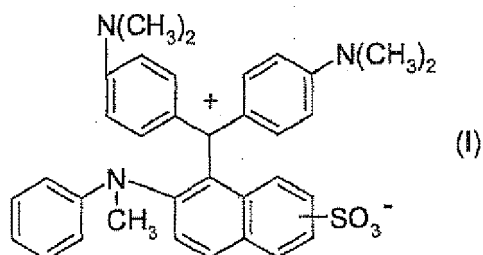


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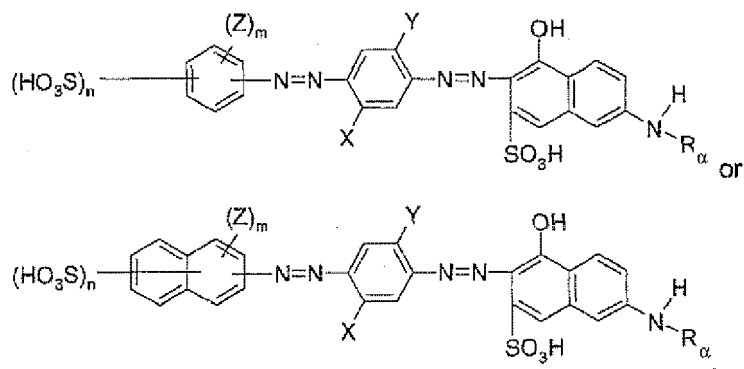


and

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- A preferred embodiment of the present invention is a composition comprising
 at least one phthalocyanine compound and
 5 at least one azo dyestuff of formulae



wherein

- X and Y, independently of one another, are each hydrogen; C₁-C₄-alkyl or C₁-C₄-alkoxy,
 10 R_α is hydrogen or aryl,
 Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,
 n is 1 or 2 and
 m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or
 at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I),
 15 which produces a relative hue angle of 220 – 320° and wherein the dyestuff component is
 degraded when the composition is exposed to light.

- A more preferred embodiment of the present invention is a composition comprising
 at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or
 20 (7), and
 at least one azo dyestuff of formula (A), (B), and/or (C) and/or
 at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I),

- 17 -

which produces a relative hue angle of $220 - 320^\circ$ and wherein the dyestuff component is degraded when the composition is exposed to sunlight.

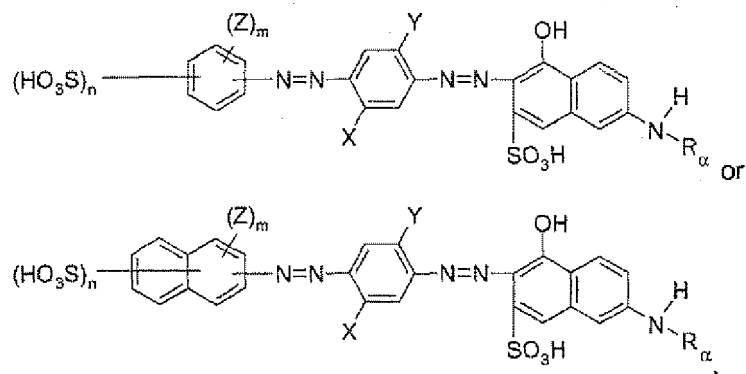
The composition, which comprises at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, can be used in solid or liquid formulation.

A further embodiment is a solid formulation comprising a composition, which comprises at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff.

10

A preferred embodiment of the present invention is a solid formulation comprising at least one composition, which comprises at least one phthalocyanine compound and at least one azo dyestuff of formulae

15



wherein

X and Y , independently of one another, are each hydrogen; $\text{C}_1\text{-C}_4\text{-alkyl}$ or $\text{C}_1\text{-C}_4\text{-alkoxy}$, R_α is hydrogen or aryl,

Z is $\text{C}_1\text{-C}_4\text{-alkyl}$; $\text{C}_1\text{-C}_4\text{-alkoxy}$; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I).

A more preferred embodiment of the present invention is a solid formulation comprising at least one composition, which comprises at least one phthalocyanine compound and at least one azo dyestuff of formula (A), (B), and/or (C) and/or

- 18 -

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I).

A preferred embodiment of the present invention is a solid formulation comprising a composition, which comprises

- 5 at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and
 at least one azo dyestuff of formula (A), (B), and/or (C) and/or
 at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I).
- 10 Granulates are preferred as solid formulation.

The present invention also relates to granulates comprising

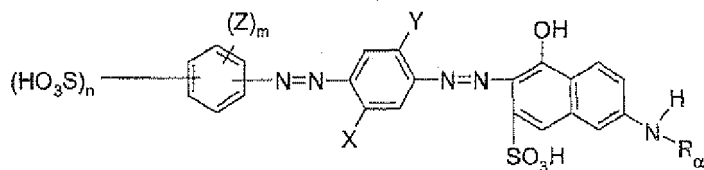
- a) from 2 to 75 % by weight (wt-%) of at least one composition comprising
 at least one water-soluble phthalocyanine
 15 compound and at least one azo dyestuff and/or at
 least one triphenylmethane dyestuff as defined
 above, based on the total weight of the granulate,
 b) from 10 to 95 wt-% of at least one further additive, based on the total
 weight of the granulate, and
 20 c) from 0 to 15 wt-% water, based on the total weight of the granulate.

The sum of the wt-% of components a) – c) is always 100 %.

- 25 The preferences for the phthalocyanines, for the azo and triphenylmethane dyestuffs as
 defined above also apply for the solid and/or granular formulation.

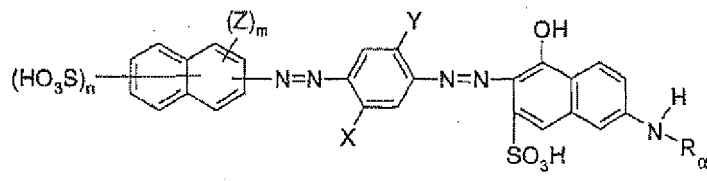
A preferred embodiment of the present invention relates to granulates comprising

- a) from 2 to 75 wt-% of the composition comprising
 at least one phthalocyanine compound and
 30 at least one azo dyestuff of formulae



- 19 -

or



wherein

X and Y, independently of one another, are each hydrogen;

C₁-C₄-alkyl or C₁-C₄-alkoxy,R_α is hydrogen or aryl,Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the granulate,

b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the granulate, and

c) from 0 to 15 wt-% water, based on the total weight of the granulate.

A more preferred embodiment of the present invention relates to granulates comprising

a) from 2 to 75 wt-% of at least one composition comprising

at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and

at least one azo dyestuff of formula (A), (B), and/or (C) and/or

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the granulate,

b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the granulate, and

c) from 0 to 15 wt-% water, based on the total weight of the granulate.

The granulates according to the invention can be encapsulated or not.

- 20 -

Encapsulating materials include especially water-soluble and water-dispersible polymers and waxes. Of those materials, preference is given to polyethylene glycols, polyamides, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, gelatin, hydrolysed polyvinyl acetates, copolymers of vinylpyrrolidone and vinyl acetate, and also polyacrylates, paraffins, fatty acids, copolymers of ethyl acrylate with methacrylate and methacrylic acid, and poly-methacrylates.

The granulates according to the invention contain from 2 to 75 wt-%, preferably from 2 to 60 wt-%, especially from 5 to 55 wt-%, of component a), based on the total weight of the granulate.

The granulates in the formulations according to the invention contain from 10 to 95 wt-%, preferably from 10 to 85 wt-%, especially from 10 to 80 wt-%, of at least one further additive (component c)), based on the total weight of the granulate.

Such further additives may be anionic or non-ionic dispersing agents; water-soluble organic polymers; inorganic salt; low-molecular-weight organic acid or a salt thereof; wetting agents; disintegrants such as, for example, powdered or fibrous cellulose, microcrystalline cellulose; fillers such as, for example, dextrin; water-insoluble or water-soluble dyes or pigments; and also dissolution accelerators and optical brighteners. Aluminium silicates such as zeolites, and also compounds such as talc, kaolin, TiO_2 , SiO_2 or magnesium trisilicate may also be used in small amounts.

The anionic dispersing agents used are, for example, the commercially available water-soluble anionic dispersing agents for dyes, pigments etc.

The following products, especially, come into consideration: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with unsubstituted or chlorinated biphenyls or biphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkylnaphthalenesulfonic acids, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkyl polyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyl diglycol ether sulfates, sodium salts of polynaphthalene-methanesulfonates, ligno- or oxy-ligno-sulfonates or heterocyclic polysulfonic acids.

Especially suitable anionic dispersing agents are condensation products of naphthalene-sulfonic acids with formaldehyde, sodium salts of polymerised organic sulfonic acids, (mono-/di-)alkylnaphthalenesulfonates, polyalkylated polynuclear arylsulfonates, sodium salts of polymerised alkylbenzenesulfonic acid, lignosulfonates, oxylignosulfonates and
 5 condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl.

Suitable non-ionic dispersants are especially compounds having a melting point of, preferably, at least 35°C that are emulsifiable, dispersible or soluble, for example the following compounds:

- 10 1. fatty alcohols having from 8 to 22 carbon atoms, especially cetyl alcohol;
2. addition products of, preferably, from 2 to 80 mol of alkylene oxide, especially ethylene oxide, wherein some of the ethylene oxide units may have been replaced by substituted epoxides, such as styrene oxide and/or propylene oxide, with higher unsaturated or saturated monoalcohols, fatty acids, fatty amines or fatty amides having from 8 to 22
 15 carbon atoms or with benzyl alcohols, phenyl phenols, benzyl phenols or alkyl phenols, the alkyl radicals of which have at least 4 carbon atoms;
3. alkylene oxide, especially propylene oxide, condensation products (block polymers);
4. ethylene oxide/propylene oxide adducts with diamines, especially ethylenediamine;
5. reaction products of a fatty acid having from 8 to 22 carbon atoms and a primary or
 20 secondary amine having at least one hydroxy-lower alkyl or lower alkoxy-lower alkyl group, or alkylene oxide addition products of such hydroxyalkyl-group-containing reaction products;
6. sorbitan esters, preferably with long-chain ester groups, or ethoxylated sorbitan esters, such as polyoxyethylene sorbitan monolaurate having from 4 to 10 ethylene oxide units or
 25 polyoxyethylene sorbitan trioleate having from 4 to 20 ethylene oxide units;
7. addition products of propylene oxide with a tri- to hexa-hydric aliphatic alcohol having from 3 to 6 carbon atoms, e.g. glycerol or pentaerythritol; and
8. fatty alcohol polyglycol mixed ethers, especially addition products of from 3 to 30 mol of ethylene oxide and from 3 to 30 mol of propylene oxide with aliphatic monoalcohols
 30 having from 8 to 22 carbon atoms.

Especially suitable non-ionic dispersants are surfactants of formula



- 22 -

wherein

R_{20} is C_8 - C_{22} alkyl or C_8 - C_{18} alkenyl;

R_{21} is hydrogen; C_1 - C_4 alkyl; a cycloaliphatic radical having at least 6 carbon atoms or benzyl;

- 5 "alkylene" is an alkylene radical having from 2 to 4 carbon atoms and
 n is a number from 1 to 60.

The substituents R_{20} and R_{21} in formula (8) are advantageously each the hydrocarbon radical of an unsaturated or, preferably, saturated aliphatic monoalcohol having from 8 to 22 carbon
 10 atoms. The hydrocarbon radical may be straight-chain or branched. R_{20} and R_{21} are preferably each independently of the other an alkyl radical having from 9 to 14 carbon atoms.

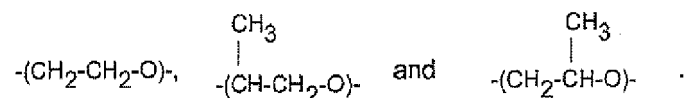
Aliphatic saturated monoalcohols that come into consideration include natural alcohols, e.g. lauryl alcohol, myristyl alcohol, cetyl alcohol or stearyl alcohol, and also synthetic alcohols,
 15 e.g. 2-ethylhexanol, 1,1,3,3-tetramethylbutanol, octan-2-ol, isononyl alcohol, trimethylhexanol, trimethylnonyl alcohol, decanol, C_9 - C_{11} oxo-alcohol, tridecyl alcohol, isotridecyl alcohol and linear primary alcohols (Alfols) having from 8 to 22 carbon atoms. Some examples of such Alfols are Alfol (8-10), Alfol (9-11), Alfol (10-14), Alfol (12-13) and Alfol (16-18). ("Alfol" is a registered trade mark).

20

Unsaturated aliphatic monoalcohols are, for example, dodecenyl alcohol, hexadecenyl alcohol and oleyl alcohol.

The alcohol radicals may be present singly or in the form of mixtures of two or more
 25 components, e.g. mixtures of alkyl and/or alkenyl groups that are derived from soybean fatty acids, palm kernel fatty acids or tallow oils.

(Alkylene-O) chains are preferably divalent radicals of the formulae



30 Examples of a cycloaliphatic radical are cycloheptyl, cyclooctyl and preferably cyclohexyl. As non-ionic dispersants there come into consideration preferably surfactants of formula

- 23 -



wherein

R_{22} is $\text{C}_8\text{-C}_{22}$ alkyl;

R_{23} is hydrogen or $\text{C}_1\text{-C}_4$ alkyl;

$\text{Y}_1, \text{Y}_2, \text{Y}_3$ and Y_4 are each independently of the others hydrogen; methyl or ethyl;

5 n_2 is a number from 0 to 8; and

n_3 is a number from 2 to 40.

Further important non-ionic dispersants correspond to formula



wherein

10 R_{24} is $\text{C}_8\text{-C}_{14}$ alkyl;

R_{25} is $\text{C}_1\text{-C}_4$ alkyl;

$\text{Y}_5, \text{Y}_6, \text{Y}_7$ and Y_8 are each independently of the others hydrogen; methyl or ethyl, one of the radicals Y_5, Y_6 and one of the radicals Y_7, Y_8 always being hydrogen; and

n_4 and n_5 are each independently of the other an integer from 4 to 8.

15

The non-ionic dispersants of formulae (8) to (10) can also be used in the form of mixtures.

For example, as surfactant mixtures there come into consideration non-end-group-terminated fatty alcohol ethoxylates of formula (8), e.g. compounds of formula (8) wherein

R_{20} is $\text{C}_8\text{-C}_{22}$ alkyl,

20 R_{21} is hydrogen and

the alkylene-O chain is the radical $-(\text{CH}_2\text{-CH}_2\text{-O})\text{-}$

and also end-group-terminated fatty alcohol ethoxylates of formula (10).

Examples of non-ionic dispersants of formulae (8), (9) and (10) include reaction products of a

25 $\text{C}_{10}\text{-C}_{13}$ fatty alcohol, e.g. a C_{13} oxo-alcohol, with from 3 to 10 mol of ethylene oxide, propylene oxide and/or butylene oxide or the reaction product of one mol of a C_{13} fatty alcohol with 6 mol of ethylene oxide and 1 mol of butylene oxide, it being possible for the addition products each to be end-group-terminated with $\text{C}_1\text{-C}_4$ alkyl, preferably methyl or butyl.

Such dispersants can be used singly or in the form of mixtures of two or more dispersants.

Instead of or in addition to the dispersing agent or agents, the granulates according to the invention may comprise a water-soluble organic polymer, which may also have dispersing properties. Such polymers may be used singly or as mixtures of two or more polymers. As
5 water-soluble polymers (which may, but need not, have film-forming properties), there come into consideration, for example, gelatins, polyacrylates, polymethacrylates, copolymers of ethyl acrylate, methyl methacrylate and methacrylic acid (ammonium salt), polyvinylpyrrolidones, vinylpyrrolidones, vinyl acetates, copolymers of vinylpyrrolidone with
10 long-chain olefins, poly(vinylpyrrolidone/dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropyl methacrylamides, copolymers of vinylpyrrolidone/dimethylaminopropyl acrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methacrylates, terpolymers of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and
15 methacrylamidopropyltrimethylammonium chloride, terpolymers of caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of styrene and acrylic acid, polycarboxylic acids, polyacrylamides, carboxymethyl cellulose, hydroxymethyl cellulose, polyvinyl alcohols, hydrolysed and non-hydrolysed polyvinyl acetate, copolymers of maleic acid with unsaturated hydrocarbons and also mixed polymerisation products of the
20 mentioned polymers. Further suitable substances are polyethylene glycol (MW = 2000 – 20 000), copolymers of ethylene oxide with propylene oxide (MW > 3500), condensation products (block polymerisation products) of alkylene oxide, especially propylene oxide, copolymers of vinylpyrrolidone with vinyl acetate, ethylene oxide-propylene oxide addition products with diamines, especially ethylenediamine, polystyrenesulfonic acid, polyethylene-sulfonic acid, copolymers of acrylic acid with sulfonated styrenes, gum arabic, hydroxypropyl
25 methylcellulose, sodium carboxymethyl cellulose, hydroxypropyl methylcellulose phthalate, maltodextrin, starch, sucrose, lactose, enzymatically modified and subsequently hydrated sugars, as are obtainable under the name "Isomalt", cane sugar, polyaspartic acid and tragacanth.

30

Among those water-soluble organic polymers, special preference is given to carboxymethyl cellulose, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, gelatins, hydrolysed polyvinyl acetates, copolymers of vinylpyrrolidone and vinyl acetate, maltodextrins, polyaspartic acid and also polyacrylates and polymethacrylates.

- 25 -

For use as inorganic salts there come into consideration carbonates, hydrogen carbonates, phosphates, polyphosphates, sulfates, silicates, sulfites, borates, halides and pyrophosphates, preferably in the form of alkali metal salts. Preference is given to water-soluble salts such as, for example, alkali metal chlorides, alkali phosphates, alkali carbonates, alkali polyphosphates and alkali sulfates and water-soluble salts used in washing agent and/or washing agent additive formulations.

There come into consideration as low-molecular-weight acids, for example, mono- or polycarboxylic acids. Of special interest are aliphatic carboxylic acids, especially those having a total number of from 1 to 12 carbon atoms. Preferred acids are aliphatic C₁-C₁₂-mono- or -poly-carboxylic acids, the monocarboxylic acids being especially those having at least 3 carbon atoms in total. As substituents of the carboxylic acids there come into consideration, for example, hydroxy and amino, especially hydroxy. Special preference is given to aliphatic C₂-C₁₂polycarboxylic acids, especially aliphatic C₂-C₆polycarboxylic acids. Very special preference is given to hydroxy-substituted aliphatic C₂-C₆polycarboxylic acids. These compounds may be used in the form of the free acid or a salt, especially an alkali salt.

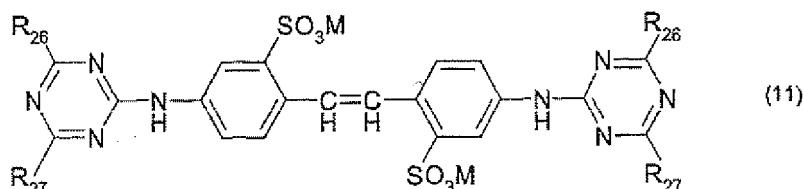
There may also be used aminopolycarboxylates (e.g. sodium ethylenediaminetetraacetate), phytates, phosphonates, aminopolyphosphonates (e.g. sodium ethylenediaminetetraphosphonate), aminoalkylenepoly(alkylenephosphonates), polyphosphonates, polycarboxylates or water-soluble polysiloxanes.

As examples of low-molecular-weight organic acids and salts thereof there may be mentioned oxalic acid, tartaric acid, acetic acid, propionic acid, succinic acid, maleic acid, citric acid, formic acid, gluconic acid, p-toluenesulfonic acid, terephthalic acid, benzoic acid, phthalic acid, acrylic acid and polyacrylic acid.

The optical brighteners may be selected from a wide range of chemical types such as 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acids, 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acids, 4,4'-(diphenyl)-stilbenes, 4,4'-distyryl-biphenyls, 4-phenyl-4'-benzoxazolyl-stilbenes, stilbenyl-naphthotriazoles, 4-styryl-stilbenes, bis-(benzoxazol-2-yl) derivatives, bis-(benzimidazol-2-yl) derivatives, coumarines, pyrazolines, naphthalimides, triazinyl-pyrenes, 2-styryl-benzoxazole- or -naphthoxazole derivatives, benzimidazole-benzofuran derivatives or oxanilide derivatives.

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With particular reference to the use of a composition, which is an aqueous textile finishing composition, preferred 4,4'-bis-(triazinylamino)-stilbene-2,2'-disulfonic acids are those having the formula (11):



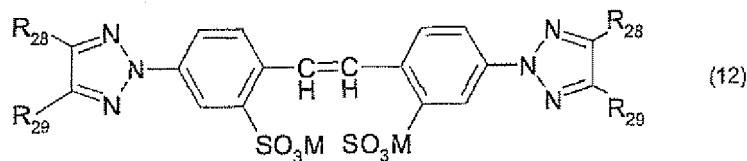
5 in which

R_{26} and R_{27} , independently of one another, are phenyl; mono- or disulfonated phenyl; phenylamino; mono- or disulfonated phenylamino; morpholino; $-N(CH_2CH_2OH)_2$; $-N(CH_3)(CH_2CH_2OH)$; $-NH_2$; $-N(C_1-C_4alkyl)_2$; $-OCH_3$; $-Cl$; $-NH-CH_2CH_2SO_3H$ or $-NH-CH_2CH_2OH$; and

10 M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- C_1-C_4 -alkylammonium; mono-, di- or tri- C_1-C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C_1-C_4 -alkyl and C_1-C_4 -hydroxyalkyl groups.

Especially preferred compounds of formula (11) are those in which each R_{26} is 2,5-
 15 disulfophenyl and each R_{27} is morpholino; or each R_{26} is 2,5-disulfophenyl and each R_{27} is $N(C_2H_5)_2$; or each R_{26} is 3-sulfophenyl and each R_{27} is $NH(CH_2CH_2OH)$ or $N(CH_2CH_2OH)_2$; or each R_{26} is 4-sulfophenyl and each R_{27} is $N(CH_2CH_2OH)_2$; and, in each case, the sulfo group is SO_3M in which M is sodium.

20 Preferred 4,4'-bis-(triazol-2-yl)stilbene-2,2'-disulfonic acids are those having the formula (12):



in which

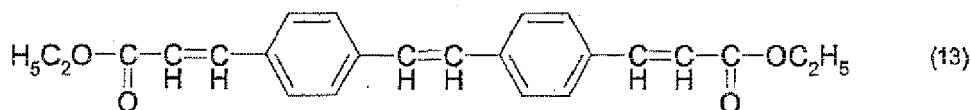
R_{28} and R_{29} , independently of one another, are H; C_1-C_4 -alkyl; phenyl or monosulfonated phenyl; and

25 M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- C_1-C_4 -alkylammonium; mono-, di- or tri- C_1-C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C_1-C_4 -alkyl and C_1-C_4 -hydroxyalkyl groups.

- 27 -

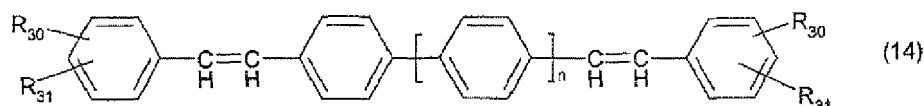
Especially preferred compounds of formula (12) are those in which R_{28} is phenyl, R_{29} is H and M is sodium.

One preferred 4,4'-(diphenyl)-stilbene is that having the formula (13):



5

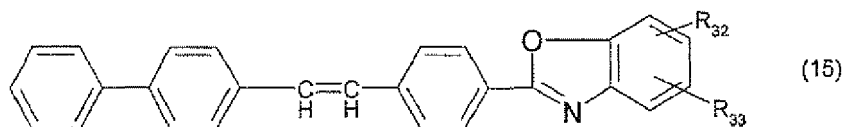
Preferably, 4,4'-distyryl-biphenyls used are those of formula (14):



in which

- 10 R_{30} and R_{31} , independently of one another, are H; $-\text{SO}_3\text{M}$; $-\text{SO}_2\text{N}(\text{C}_1-\text{C}_4\text{-alkyl})_2$; $\text{O}-(\text{C}_1-\text{C}_4\text{-alkyl})$; CN; Cl; $\text{COO}(\text{C}_1-\text{C}_4\text{-alkyl})$; $\text{CON}(\text{C}_1-\text{C}_4\text{-alkyl})_2$ or $\text{O}(\text{CH}_2)_3\text{N}^{(+)}(\text{CH}_3)_2\text{An}^{(-)}$ in which $\text{An}^{(-)}$ is an anion of an organic or inorganic acid, in particular a formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, sulfonate, dimethyl or diethyl phosphite anion, or a mixture thereof,
- 15 n is 0 or 1 and
- M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- $\text{C}_1-\text{C}_4\text{-alkylammonium}$; mono-, di- or tri- $\text{C}_1-\text{C}_4\text{-hydroxyalkylammonium}$ or ammonium that is di- or tri-substituted with by a mixture of $\text{C}_1-\text{C}_4\text{-alkyl}$ and $\text{C}_1-\text{C}_4\text{-hydroxyalkyl}$ groups.
- 20 Especially preferred compounds of formula (14) are those in which n is 1 and each R_{30} is a $-\text{SO}_3\text{M}$ group in which M is sodium and each R_{31} is H, or each R_{31} is $-\text{O}(\text{CH}_2)_3\text{N}^{(+)}(\text{CH}_3)_2\text{An}^{(-)}$ in which $\text{An}^{(-)}$ is acetate.

Preferred 4-phenyl-4'-benzoxazolyl-stilbenes have the formula (15):



25

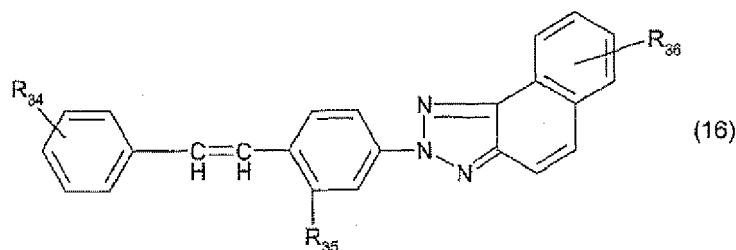
in which

R_{32} and R_{33} , independently of one another, are H; Cl; $\text{C}_1-\text{C}_4\text{-alkyl}$ or $-\text{SO}_2-\text{C}_1-\text{C}_4\text{-alkyl}$.

- 28 -

An especially preferred compound of formula (15) is that in which R_{32} is 4-CH₃ and R_{33} is 2-CH₃.

Preferably, stilbenyl-naphthotriazoles used are those of formula (16):



5

in which

R_{34} is H or Cl;

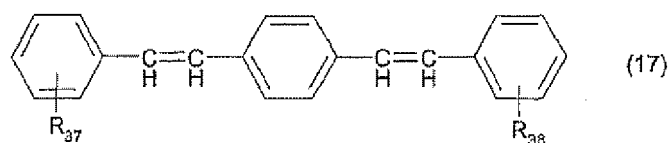
R_{35} is -SO₃M; -SO₂N(C₁-C₄-alkyl)₂; -SO₂O-phenyl or -CN;

R_{36} is H or -SO₃M; and

- 10 M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra-C₁-C₄-alkylammonium; mono-, di- or tri-C₁-C₄-hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C₁-C₄-alkyl and C₁-C₄-hydroxyalkyl groups.

- Especially preferred compounds of formula (16) are those in which R_{34} and R_{35} are H and R_{36} is 2-SO₃M in which M is Na.
- 15

Preferably, 4-styryl-stilbenes used are those of formula:



in which

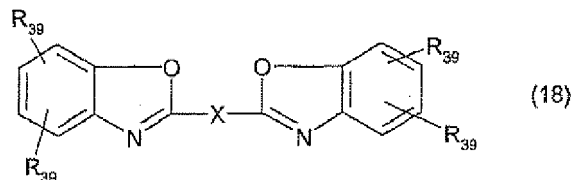
- 20 R_{37} and R_{38} , independently of one another, are H; -SO₃M; -SO₂N(C₁-C₄-alkyl)₂; -O-(C₁-C₄-alkyl); -CN; -Cl; -COO(C₁-C₄-alkyl); -CON(C₁-C₄-alkyl)₂ or -O(CH₂)₃N⁽⁺⁾(CH₃)₂An⁽⁻⁾ in which An⁽⁻⁾ is an anion of an organic or inorganic acid, in particular a formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, sulfonate, dimethyl or diethyl phosphite anion, or a mixture thereof.

25

- 29 -

Especially preferred compounds of formula (17) are those in which each of R_{37} and R_{38} is 2-cyano; $2-SO_3M$ in which M is sodium or $O(CH_2)_3N^{(+)}(CH_3)_2An^{(-)}$ in which $An^{(-)}$ is acetate.

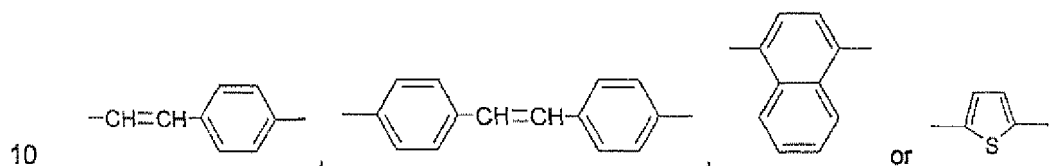
Preferred bis-(benzoxazol-2-yl) derivatives are those of formula (18):



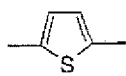
in which

R_{39} , independently of one another, is H; $C(CH_3)_3$; $C(CH_3)_2$ -phenyl; C_1 - C_4 -alkyl or COO - C_1 - C_4 -alkyl, and

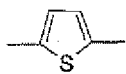
X is $-CH=CH-$ or a group of formula:



Especially preferred compounds of formula (18) are those in which each R_{39} is H and X is

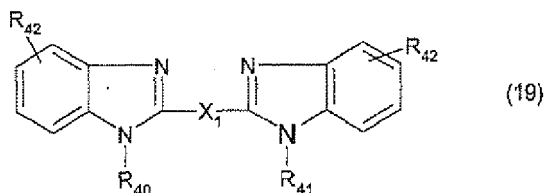


; or one group R_{39} in each ring is 2-methyl and the other R_{39} is H and X is $-CH=CH-$; or one group R_{39} in each ring is 2- $C(CH_3)_3$ and the other R_{39} is H and X is



15

Preferred bis-(benzimidazol-2-yl) derivatives are those of formula (19):



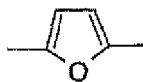
in which

20 R_{40} and R_{41} , independently of one another, are H; C_1 - C_4 -alkyl or CH_2CH_2OH ;

R_{42} is H or SO_3M ;

- 30 -

X_1 is $-\text{CH}=\text{CH}-$ or a group of formula:



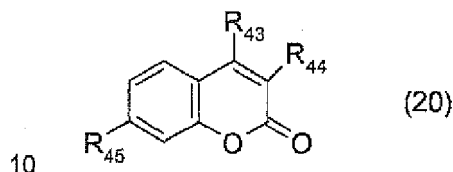
and

M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- C_1 - C_4 -alkylammonium; mono-, di- or tri- C_1 - C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C_1 - C_4 -alkyl and C_1 - C_4 -hydroxyalkyl groups.

5

Especially preferred compounds of formula (19) are those in which R_{40} and R_{41} are each H, R_{42} is SO_3M in which M is sodium and X_1 is $-\text{CH}=\text{CH}-$.

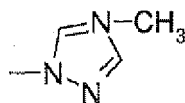
Preferred coumarines are those of formula:



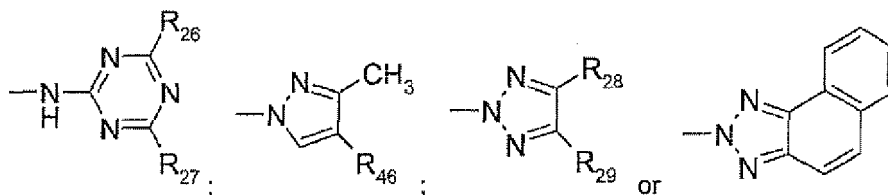
in which

R_{43} is H; $-\text{Cl}$ or $-\text{CH}_2\text{COOH}$,

R_{44} is H; phenyl; $-\text{COO}-\text{C}_1$ - C_4 -alkyl or a group of formula:



15 and R_{45} is $-\text{O}-\text{C}_1$ - C_4 -alkyl; $-\text{N}(\text{C}_1$ - C_4 -alkyl) $_2$; $-\text{NH}-\text{CO}-\text{C}_1$ - C_4 -alkyl or a group of formula:

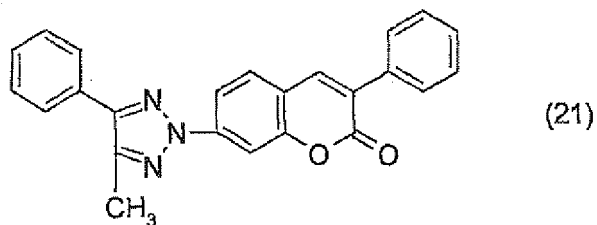


in which R_{26} , R_{27} , R_{28} and R_{29} have their previous significance and

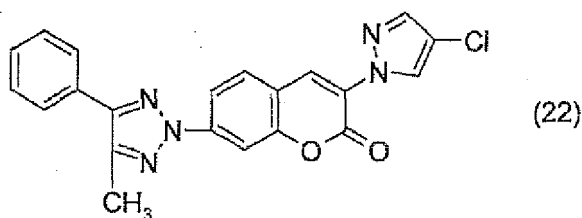
R_{46} is H; C_1 - C_4 -alkyl or phenyl.

20 Especially preferred compounds of formula (20) are those having the formula (21) and (22):

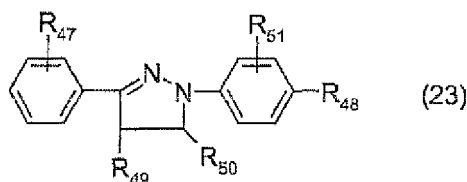
- 31 -



or



Preferably, pyrazolines used are those having the formula (23):



5

in which

R_{47} is H; -Cl or $-N(C_1-C_4\text{-alkyl})_2$,

R_{48} is H; -Cl; $-SO_3M$; $-SO_2NH_2$; $-SO_2NH-(C_1-C_4\text{-alkyl})$; $-COO-C_1-C_4\text{-alkyl}$; $-SO_2-C_1-C_4\text{-alkyl}$; $-SO_2NHCH_2CH_2CH_2N^{(+)}(CH_3)_3$ or $SO_2CH_2CH_2N^{(+)}H(C_1-C_4\text{-alkyl})_2 An^{(-)}$,

10 R_{49} and R_{50} are the same or different and each is H; $C_1-C_4\text{-alkyl}$ or phenyl,

R_{51} is H or -Cl,

$An^{(-)}$ is an anion of an organic or inorganic acid, in particular a formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, sulfonate, dimethyl or diethyl phosphite anion, or a mixture thereof and

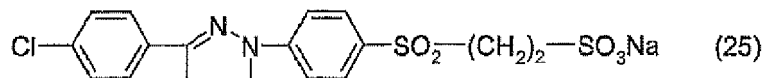
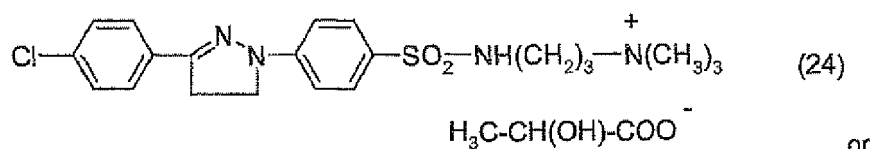
15 M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- $C_1-C_4\text{-alkylammonium}$; mono-, di- or tri- $C_1-C_4\text{-hydroxyalkylammonium}$ or ammonium that is di- or tri-substituted with by a mixture of $C_1-C_4\text{-alkyl}$ and $C_1-C_4\text{-hydroxyalkyl}$ groups.

Especially preferred compounds of formula (23) are those in which R_{47} is -Cl; R_{48} is

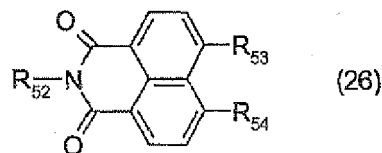
$-SO_2CH_2CH_2N^{(+)}H(C_1-C_4\text{-alkyl})_2 An^{(-)}$ in which $An^{(-)}$ is phosphite and R_{49} , R_{50} and R_{51} are each

20 H; or those those having the formula (24) and (25):

- 32 -



Preferred naphthalimides are those of formula (26):



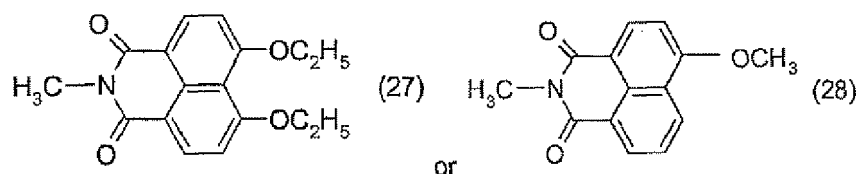
5

in which R₅₂ is C₁-C₄-alkyl or -CH₂CH₂CH₂N⁽⁺⁾(CH₃)₃;

R₅₃ and R₅₄, independently of one another, are -O-C₁-C₄-alkyl; -SO₃M or -NH-CO-C₁-C₄-alkyl; and

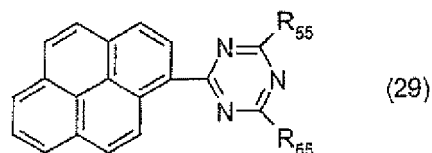
M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra-C₁-C₄-alkylammonium; mono-, di- or tri-C₁-C₄-hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C₁-C₄-alkyl and C₁-C₄-hydroxyalkyl groups.

Especially preferred compounds of formula (26) are those having the formula (27) and (28):



15

Preferred triazinyl-pyrenes used are those of formula (29):



in which

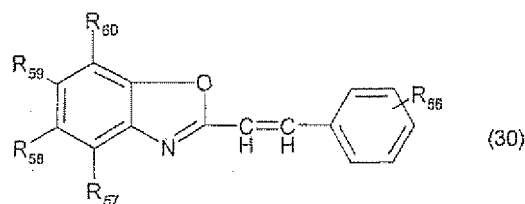
each R₅₅, independently of one another, is C₁-C₄-alkoxy.

20

Especially preferred compounds of formula (29) are those in which each R₅₅ is methoxy.

- 33 -

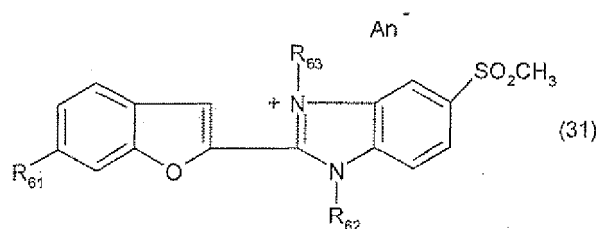
Preferred 2-styryl-benzoxazole- or -naphthoxazole derivatives are those having the formula (30):



in which

- 5 R_{66} is -CN; -Cl; -COO-C₁-C₄-alkyl or phenyl;
 R_{57} and R_{59} are the atoms required to form a fused benzene ring or
 R_{58} and R_{60} , independently of one another, are H or C₁-C₄-alkyl; and
 R_{59} is H; C₁-C₄-alkyl or phenyl.
- 10 Especially preferred compounds of formula (30) are those in which R_{59} is a 4-phenyl group and each of R_{57} to R_{60} is H.

Preferred benzimidazole-benzofuran derivatives are those having the formula (31):

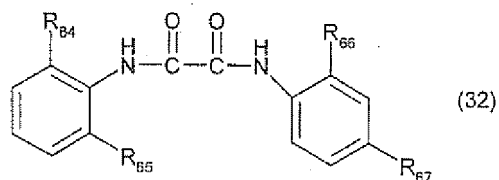


- 15 in which
 R_{61} is C₁-C₄-alkoxy;
 R_{62} and R_{63} , independently of one another, are C₁-C₄-alkyl; and
 $An^{(-)}$ is an anion of an organic or inorganic acid, in particular a formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, sulfonate, dimethyl or diethyl
20 phosphite anion, or a mixture thereof.

A particularly preferred compound of formula (31) is that in which R_{61} is methoxy, R_{62} and R_{63} are each methyl and $An^{(-)}$ is methane sulfonate.

- 25 Preferred oxanilide derivatives include those having the formula (32):

- 34 -



in which

R_{64} is C_1 - C_4 alkoxy,

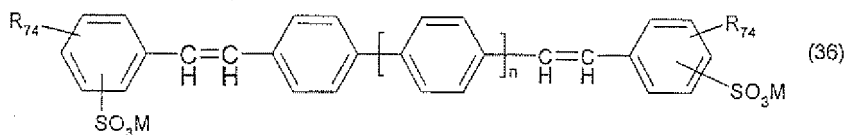
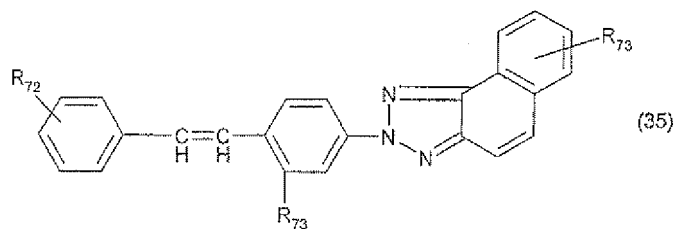
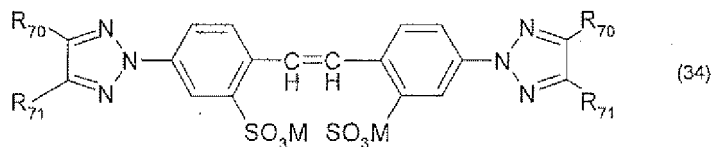
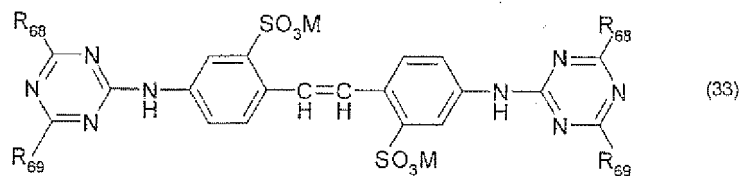
R_{66} is C_1 - C_4 alkyl; C_1 - C_4 alkyl- SO_3M or C_1 - C_4 alkoxy- SO_3M in which

- 5 M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- C_1 - C_4 -alkylammonium; mono-, di- or tri- C_1 - C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C_1 - C_4 -alkyl and C_1 - C_4 -hydroxyalkyl groups and

R_{65} and R_{67} are the same and each is hydrogen; tert. butyl or SO_3M in which M has its previous significance.

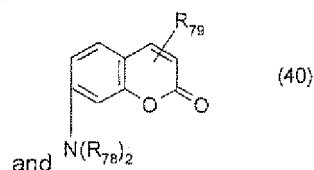
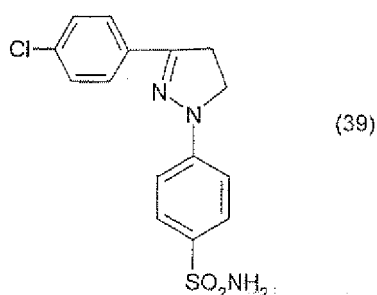
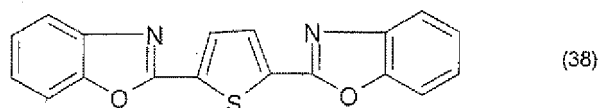
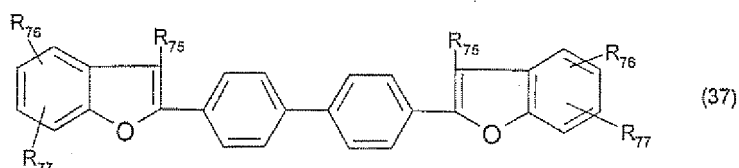
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Preferred FWA are those having one of the formulae:



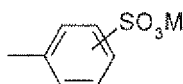
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- 35 -



in which

- 5 R_{68} and R_{69} , independently of one another, are -OH; -NH₂; -O-C₁-C₄-alkyl; -O-aryl; -NH-C₁-C₄-alkyl; -N(C₁-C₄-alkyl)₂; -N(C₁-C₄-alkyl)(C₁-C₄-hydroxyalkyl); -N(C₁-C₄-hydroxyalkyl)₂; -NH-aryl; morpholino; -S-C₁-C₄-alkyl(aryl) or Cl;
 R_{70} and R_{71} , independently of one another, are H; C₁-C₄-alkyl; phenyl or a group of formula:

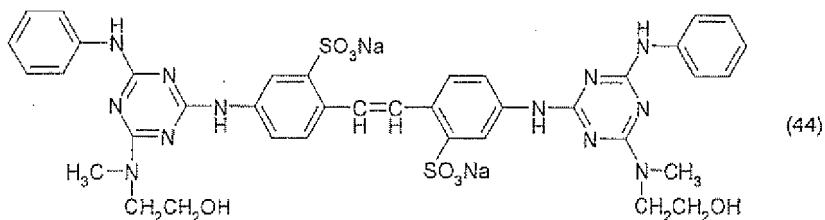
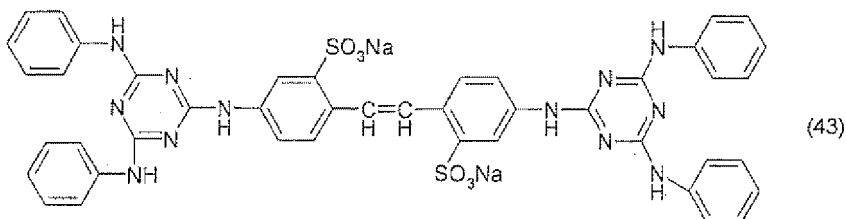
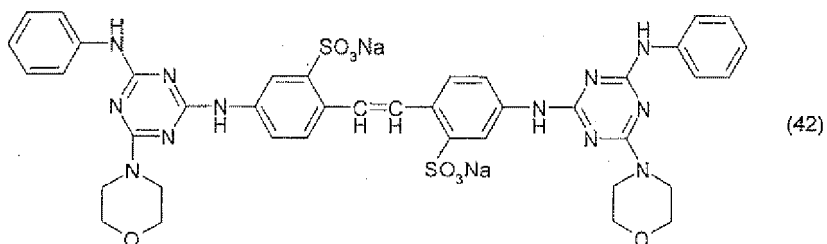
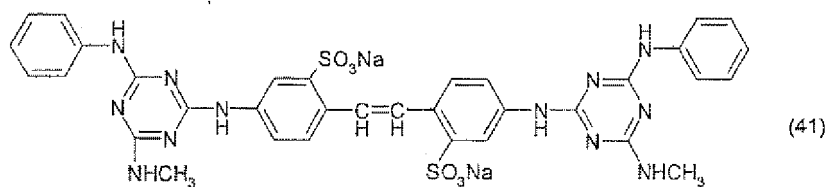


- 10 R_{72} is H; -Cl or -SO₃M;
 R_{73} is -CN; -SO₃M; -S(C₁-C₄-alkyl)₂ or -S(aryl)₂;
 R_{74} is H; -SO₃M; -O-C₁-C₄-alkyl; -CN; -Cl; -COO-C₁-C₄-alkyl; or -CON(C₁-C₄-alkyl)₂;
 R_{75} is H; C₁-C₄-alkyl; -Cl or -SO₃M;
 R_{76} and R_{77} , independently of one another, are H; C₁-C₄-alkyl; -SO₃M; -Cl or -O-C₁-C₄-alkyl;
 15 R_{78} is H or C₁-C₄-alkyl;
 R_{79} is H; C₁-C₄-alkyl; -CN; -Cl; -COO-C₁-C₄-alkyl; -CON(C₁-C₄-alkyl)₂; aryl or -O-aryl; and
 M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra-C₁-C₄-alkylammonium; mono-, di- or tri-C₁-C₄-hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C₁-C₄-alkyl and C₁-C₄-hydroxyalkyl groups and
 20 n is 0 or 1.

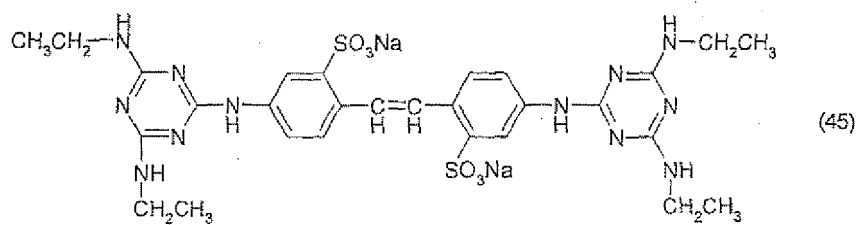
- 36 -

In the compounds of formulae (33) to (40), C₁-C₄-alkyl groups are, e.g., methyl, ethyl, n-propyl, isopropyl and n-butyl, especially methyl. Aryl groups are naphthyl or, especially, phenyl.

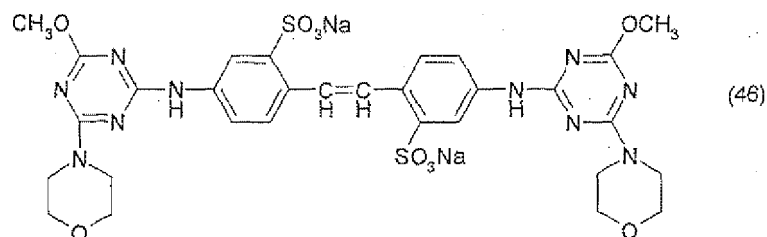
5 Specific examples of preferred compounds of formula (33) are those having the formulae:



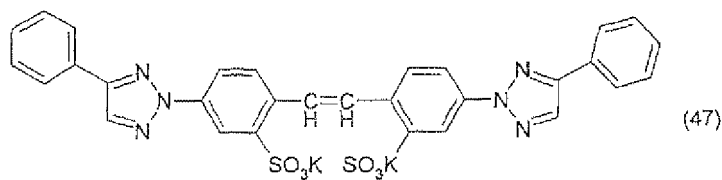
- 37 -



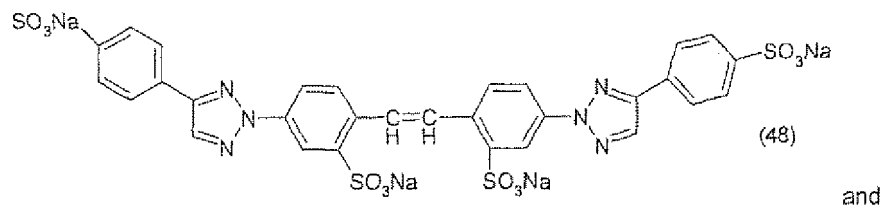
and



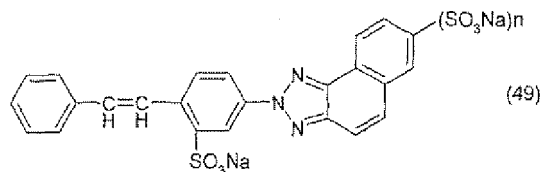
Specific preferred examples of compounds of formula (34) are those of formulae:



5



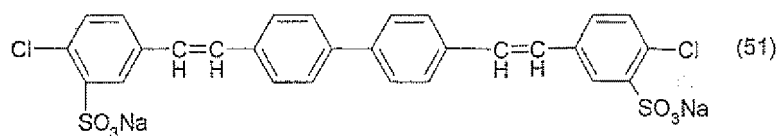
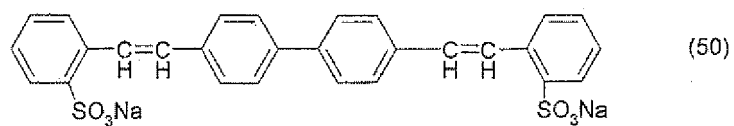
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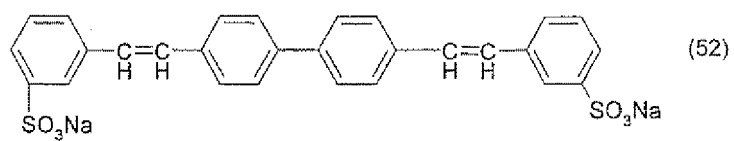
in which n has its previous significance.

10 Preferred examples of compounds of formula (36) are those having the formulae:

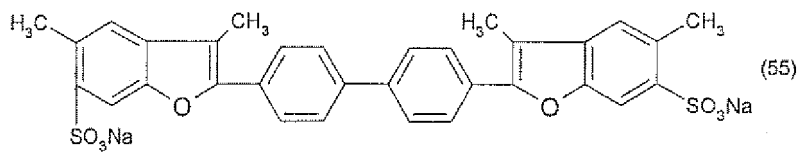
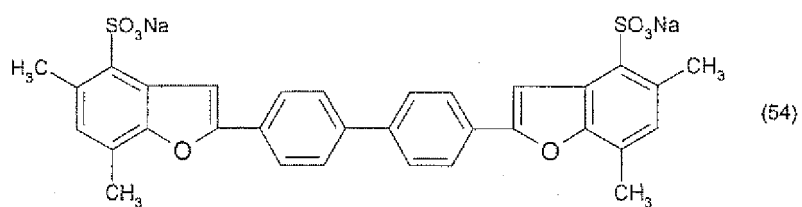
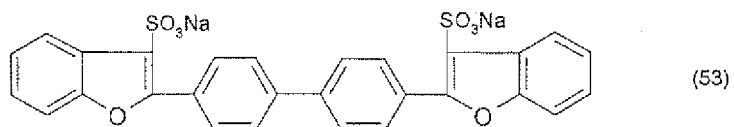
- 38 -



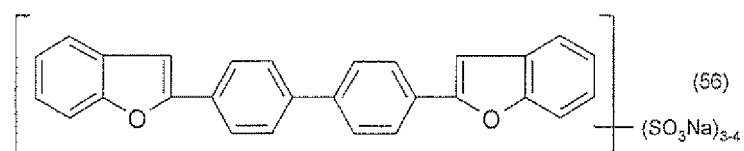
and



5 Preferred examples of compounds of formula (37) are those of formulae:



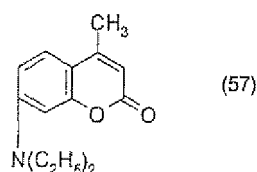
and



10

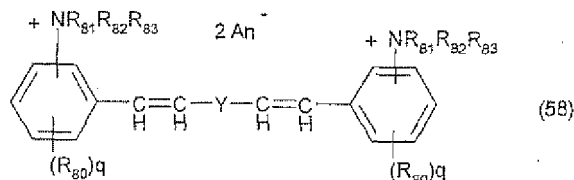
A preferred example of a compound of formula (40) is that having the formula (57):

- 39 -



The compounds of formulae (23) to (57) are known and may be obtained by known methods.

- 5 Further preferred FWA's are those of the class of cationic bistyrylphenyl fluorescent whitening agent having the formula (58):



in which

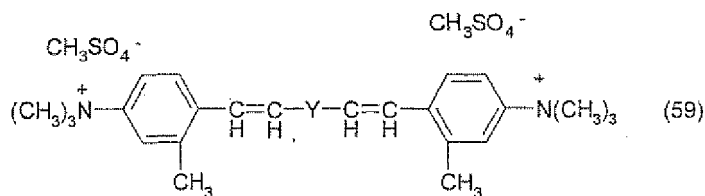
- Y is arylene, preferably 1,4-phenylene or 4,4'-diphenylene, each optionally substituted by
 10 chloro, methyl or Methoxy,
 q is 1 or 2,
 R_{80} is hydrogen; chloro; C₁-C₄-alkyl; C₁-C₄-alkoxy; cyano or C₁-C₄-alkoxycarbonyl,
 R_{81} and R_{82} are C₁-C₄-alkyl; chloroethyl; methoxyethyl; β -ethoxyethyl; β -acetoxyethyl or β -
 cyanoethyl; benzy; or phenylethyl,
 15 R_{83} is C₁-C₄-alkyl; C₂-C₃-hydroxyalkyl; β -hydroxy- γ -chloropropyl; β -cyanoethyl or C₁-C₄-
 alkoxy-carbonylethyl, and
 $An^{(-)}$ has its previous significance and is preferably the chloride; bromide; iodide;
 methosulfate; ethosulfate; benzenesulfonate or p-toluenesulfonate anion when R_{83} is C₁-C₄-
 alkyl or $An^{(-)}$ is preferably the formate; acetate; propionate or benzoate anion when R_{83} is β -
 20 hydroxy- γ -chloropropyl; β -cyanoethyl or C₁-C₄-alkoxy-carbonylethyl.

Preferred compounds of formula (58) are those in which Y is 1,4-phenylene or 4,4'-
 diphenylene; R_{80} is hydrogen; methyl or cyano; R_{81} and R_{82} are each methyl or cyano; and
 R_{83} and $An^{(-)}$ have their previously indicated preferred meanings.

25

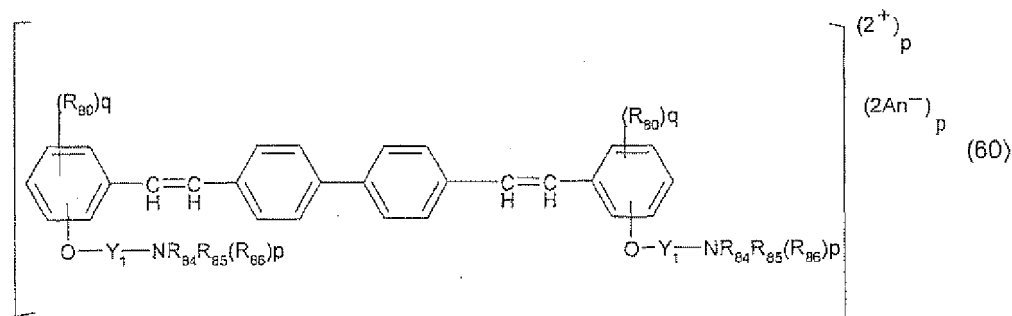
One particularly preferred compound of formula (58) is that having the formula (59):

- 40 -



The compounds of formula (58) and their production are described in US-A-4 009 193.

- 5 A further preferred class of cationic bistyrylphenyl fluorescent whitening agent is that having the formula (60):



in which

q is 1 or 2,

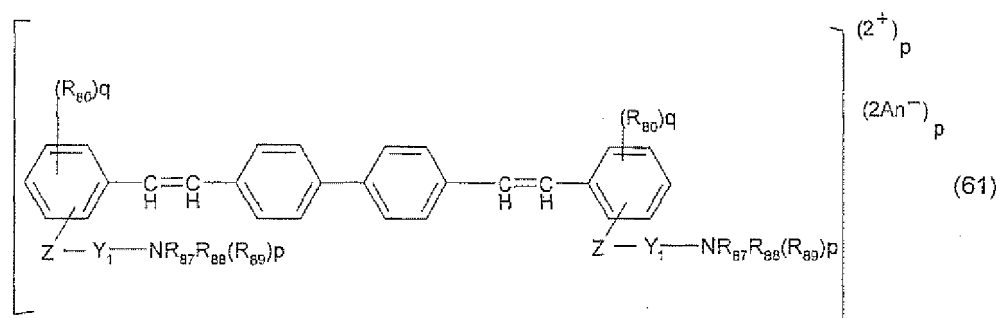
- 10 R_{90} is hydrogen; chloro; C_1 - C_4 -alkyl; C_1 - C_4 -alkoxy; cyano or C_1 - C_4 -alkoxycarbonyl;
 Y_1 is C_2 - C_4 -alkylene or hydroxypropylene;
 R_{84} is C_1 - C_4 -alkyl or, together with R_{85} and the nitrogen to which they are each attached, R_{84} forms a pyrrolidine; piperidine; hexamethyleneimine or morpholine ring;
 R_{85} is C_1 - C_4 -alkyl or, together with R_{84} and the nitrogen to which they are each attached, R_{85} forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring;
 15 R_{86} is hydrogen; C_1 - C_4 -alkyl; C_3 - C_4 -alkenyl; C_1 - C_4 -alkoxycarbonylmethyl; benzyl; C_2 - C_4 -hydroxyalkyl; C_2 - C_4 -cyanoalkyl or, together with R_{84} and R_{85} and the nitrogen atom to which they are each attached, R_{86} forms a pyrrolidine, piperidine, hexamethyleneimine or morpholine ring;
 20 $An^{(i)}$ is an anion of an organic or inorganic acid, in particular a formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, sulfonate, dimethyl or diethyl phosphite anion, or a mixture thereof, and
 p is 0 or 1.

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Preferred compounds of formula (60) are those in which q is 1; R_{80} is hydrogen, chlorine, C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy; Y_1 is $(CH_2)_2$; R_{84} and R_{85} are the same and each is methyl or ethyl; R_{86} is methyl or ethyl; p is 1; and $An^{(+)}$ is CH_3OSO_3 or $C_2H_5OSO_3$.

- 5 The compounds of formula (60) and their production are described in US-A-4 339 393.

A further preferred class of cationic bistyrylphenyl fluorescent whitening agent is that having the formula (61):



- 10 in which R_{80} , Y_1 , $An^{(+)}$, p and q have their previous significance,
 R_{87} and R_{88} , independently of one another, are C_1 - C_4 -alkyl or C_2 - C_3 -alkenyl or
 R_{87} and R_{88} , together with the nitrogen atom to which they are attached, form a pyrrolidine;
 piperidine; hexamethyleneimine or morpholine ring
 R_{89} is hydrogen; C_1 - C_4 -alkyl or C_2 - C_3 -alkenyl or
 15 R_{87} , R_{88} and R_{89} , together with the nitrogen atom to which they are attached, form a pyridine
 or picoline ring; and
 Z is sulfur; $-SO_2-$; $-SO_2NH-$; $-O-C_1-C_4$ -alkylene- $COO-$ or $-OCO-$.

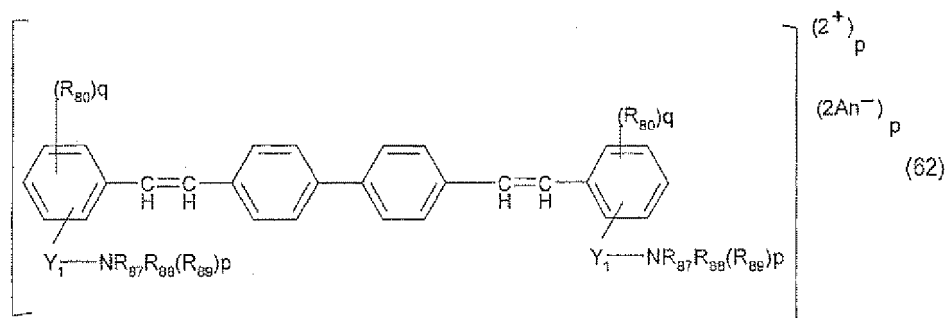
- Preferred compounds of formula (61) are those in which R_{80} is hydrogen; chloro; C_1 - C_4 -alkyl
 20 or C_1 - C_4 -alkoxy; R_{87} and R_{88} , independently of one another, are C_1 - C_4 -alkyl or, together with
 the nitrogen atom to which they are attached, form a pyrrolidine, piperidine or morpholine
 ring; R_{89} is hydrogen; C_1 - C_4 -alkyl or C_3 - C_4 -alkenyl or R_{87} , R_{88} and R_{89} , together with the
 nitrogen atom to which they are attached, form a pyridine ring; and Z is sulfur, $-SO_2-$ or
 $-SO_2NH-$.

25

The compounds of formula (61) and their production are described in US-A-4 486 352.

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A further preferred class of cationic bistyrylphenyl fluorescent whitening agent is that having the formula (62):



in which R_{80} , R_{87} , R_{88} , R_{89} , Y_1 , $An(-)$, p and q have their previous significance.

5

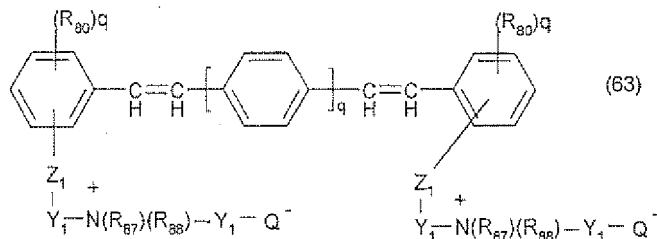
Preferred compounds of formula (62) are those in which q is 1; R_{80} is hydrogen; chloro; C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy; R_{87} and R_{88} , independently of one another, are C_1 - C_4 -alkyl or R_{87} and R_{88} together with the nitrogen atom to which they are attached, form a pyrrolidine; piperidine or morpholine ring; R_{89} is hydrogen; C_1 - C_4 -alkyl or C_3 - C_4 -alkenyl or R_{87} , R_{88} and R_{89} , together with the nitrogen atom to which they are attached, form a pyridine ring.

10

The compounds of formula (62) and their production are described in US-A-4 602 087.

One preferred class of amphoteric styrene fluorescent whitening agent is that having the formula (63):

15



in which R_{80} , R_{87} , R_{88} , Y_1 and q have their previous significance and

Z_1 is oxygen; sulfur; a direct bond; $-COO-$; $-CON(R_{90})-$ or $-SO_2N(R_{90})-$ in which

R_{90} is hydrogen; C_1 - C_4 -alkyl or cyanoethyl; and Q is $-COO-$ or $-SO_3$.

20

Preferred compounds of formula (63) are those in which Z_1 is oxygen; a direct bond;

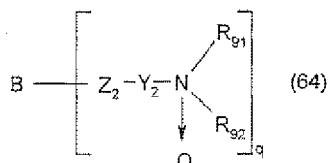
- 43 -

-CONH-; -SO₂NH- or -COO-; especially oxygen; q is 1; R₉₀ is hydrogen; C₁-C₄-alkyl; methoxy or chlorine; and R₆₇, R₉₈, Y₁ and Q have their previous significance.

The compounds of formula (63) and their production are described in US-A-4 478 598.

5

One preferred class of amine oxide fluorescent whitening agent is that having the formula:



in which

q has its previous significance;

- 10 B is a brightener radical selected from a 4,4'-distyrylbiphenyl; 4,4'-divinylstilbene, and a 1,4'-distyrylbenzene, each optionally substituted by one to four substituents selected from halogen, C₁-C₄-alkyl, C₁-C₄-hydroxyalkyl, C₁-C₄-halogenoalkyl, C₁-C₄-cyanoalkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl-C₁-C₄-alkyl, carboxy-C₁-C₄-alkyl, carb-C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkenyl, C₅-C₈-cycloalkyl, C₁-C₄-alkoxy, C₁-C₄-alkenoxy,
- 15 C₁-C₄-alkoxycarbonyl, carbamoyl, cyano, C₁-C₄-alkyl-sulfonyl, phenylsulfonyl, C₁-C₄-alkoxysulfonyl, sulfamoyl, hydroxyl, carboxyl, sulfo and trifluoromethyl;
- Z₂ is a direct bond between B and Y₂; an oxygen atom; a sulfur atom; -SO₂-; -SO₂-O-; -COO-; -CON(R₉₃)- or -SO₂N(R₉₃)- in which
- 20 R₉₃ is hydrogen or C₁-C₄-alkyl optionally substituted by halogen, cyano, hydroxyl, C₂-C₅-carbalkoxy, C₁-C₄-alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl;
- Y₂ is C₂-C₄-alkylene or C₂-C₄-alkyleneoxy-C₂-C₄-alkylene, each optionally substituted by halogen, hydroxyl, C₂-C₅-carbalkoxy, C₁-C₄-alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; and
- 25 R₉₁ and R₉₂, independently of one another, are C₅-C₈-cycloalkyl; C₁-C₄-alkyl or phenyl, each optionally substituted by halogen, hydroxyl, C₂-C₅-carbalkoxy, C₁-C₄-alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl, carbamoyl or sulfamoyl; in which, in all the carbamoyl or sulfamoyl groups, the nitrogen atom is optionally substituted by one or two
- 30 C₁-C₄-alkyl, C₁-C₄-hydroxyalkyl, C₂-C₅-cyanoalkyl, C₁-C₄-halogenoalkyl, benzyl or phenyl groups.

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Preferred brightener radicals B are those having the formula:



in which

q has its previous significance and the rings are optionally substituted as indicated above.

5

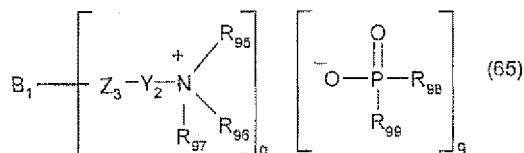
Preferably Z_2 is oxygen; $-SO_2-$ or $-SO_2N(R_{94})-$ in which R_{94} is hydrogen or C_1-C_4 -alkyl optionally substituted by hydroxyl, halogen or cyano; and R_{91} and R_{92} , independently of one another, are C_1-C_4 -alkyl optionally substituted by halogen, cyano, hydroxyl, C_1-C_4 -alkoxy, phenyl, chlorophenyl, methylphenyl, methoxyphenyl or C_2-C_5 -alkoxycarbonyl. Other preferred

10 compounds of formula (62) are those in which Z_2 is oxygen; sulfur; $-SO_2-$; $-CON(R_{94})-$ or $-SO_2N(R_{94})-$ in which R_{94} is hydrogen or C_1-C_4 -alkyl optionally substituted by hydroxyl, halogen or cyano; and Y_2 is C_1-C_4 -alkylene.

The compounds of formula (64) and their production are described in US-A-4 539 161.

15

One preferred class of cationic phosphinic acid salt fluorescent whitening agent is that having the formula (65):



in which

20 q and Y_2 have their previous significance,

B_1 is brightener radical,

Z_3 is a direct bond; $-SO_2-C_2-C_4$ -alkyleneoxy; $-SO_2-C_2-C_4$ -alkylene-COO-; $-SO_2-$; $-COO-$;

$-SO_2-C_2-C_4$ -alkylene- $CON(R_{100})-$ or $-SO_2N(R_{100})-$ in which

R_{100} is hydrogen or C_1-C_4 -alkyl optionally substituted by hydroxyl, halogen or cyano;

25 R_{95} is C_1-C_4 -alkyl or C_2-C_4 -alkenyl, each optionally substituted by halogen, cyano, hydroxy, C_1-C_4 -alkoxycarbonyl or C_1-C_4 -alkylcarbonyloxy, or R_{95} is benzyl, optionally substituted by halogen, C_1-C_4 -alkyl or C_1-C_4 -alkoxy, or R_{95} , together with R_{96} or Z_3 , forms a pyrrolidine, piperidine or morpholine radical,

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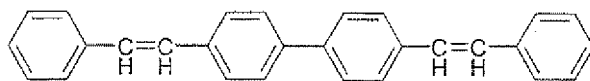
R₉₆ is C₁-C₄-alkyl or C₂-C₄-alkenyl, each optionally substituted by halogen, cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy, or R₉₅ is benzyl, optionally substituted by halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy, or R₉₆, together with R₉₅, forms a pyrrolidine, piperidine or morpholine radical,

5 R₉₇ is C₁-C₄-alkyl,

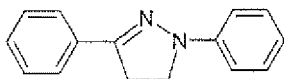
R₉₈ is hydrogen or C₁-C₄-alkyl, optionally substituted by cyano, hydroxy, C₁-C₄-alkoxycarbonyl or C₁-C₄-alkylcarbonyloxy, and

R₉₉ is C₁-C₄-alkyl.

10 Preferably, brightener radical B₁ has the formula:



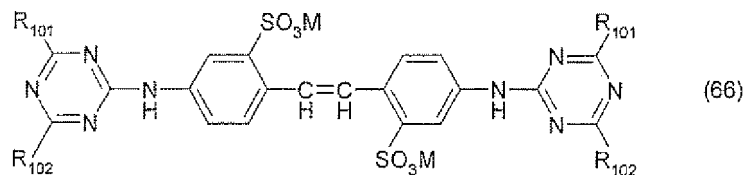
or the formula:



15 each optionally substituted by one to four substituents selected from halogen, C₁-C₄-alkyl, C₁-C₄-hydroxyalkyl, C₁-C₄-halogenoalkyl, C₁-C₄-cyanoalkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl-C₁-C₄-alkyl, carboxy-C₁-C₄-alkyl, carb-C₁-C₄-alkoxy-C₁-C₄-alkyl, C₁-C₄-alkenyl, C₅-C₈-cycloalkyl, C₁-C₄-alkoxy, C₁-C₄-alkenoxy, C₁-C₄-alkoxycarbonyl, carbamoyl, cyano, C₁-C₄-alkyl-sulfonyl, phenylsulfonyl, C₁-C₄-alkoxysulfonyl, sulfamoyl, hydroxyl, carboxyl, sulfo and
20 trifluoromethyl.

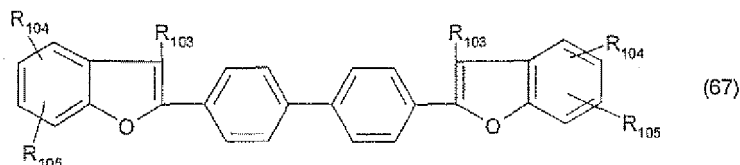
The compounds of formula (65) and their production are described in GB-A-2 023 605.

25 Preferred bis(triazinyl)diaminostilbene anionic fluorescent whitening agents for use in the present invention are those having the formula (66):

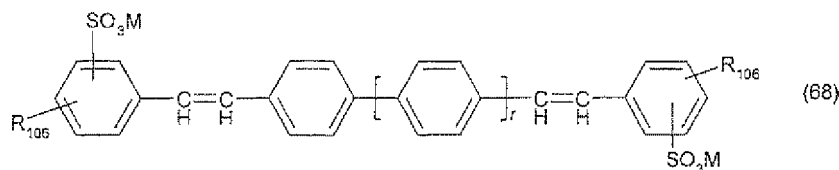


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Preferred dibenzofuranylphenyl anionic fluorescent whitening agents for use in the present invention are those having the formula (67):



- 5 Preferred anionic bistyrylphenyl fluorescent whitening agents for use in the present invention are those having the formula (68):



In the formulae (66) to (68),

- 10 R_{101} is phenyl, optionally substituted by one or two $-SO_3M$ groups,
 R_{102} is $-NH-C_1-C_4-alkyl$; $-N(C_1-C_4-alkyl)_2$; $-NH-C_1-C_4-alkoxy$; $-N(C_1-C_4-alkoxy)_2$;
 $-N(C_1-C_4-alkyl)(C_1-C_4-hydroxyalkyl)$ or $-N(C_1-C_4-hydroxyalkyl)_2$,
 R_{103} is H; $-C_1-C_4-alkyl$; $-CN$; $-Cl$ or $-SO_3M$; R_{104} and R_{105} , independently of one another, are H;
 $C_1-C_4-alkyl$; $-SO_3M$; $-CN$; $-Cl$ or $-O-C_1-C_4-alkyl$, provided that at least two of R_{103} , R_{104} and
 15 R_{105} are $-SO_3M$ and the third group has solubilising character,
 R_{106} is H; $-SO_3M$; $-O-C_1-C_4-alkyl$; $-CN$; $-Cl$; $-COO-C_1-C_4-alkyl$ or $-CON(C_1-C_4-alkyl)_2$,
 M is H; Na; K; Ca; Mg; ammonium; mono-, di-, tri- or tetra- $C_1-C_4-alkylammonium$; mono-, di-
 or tri- $C_1-C_4-hydroxyalkylammonium$ or ammonium that is di- or tri-substituted with by a
 mixture of $C_1-C_4-alkyl$ and $C_1-C_4-hydroxyalkyl$ groups and
 20 r is 0 or 1.

The compounds of formulae (66) to (68) are known and may be obtained by known methods.

Especially preferred are the non-ionic or the anionic FWA's.

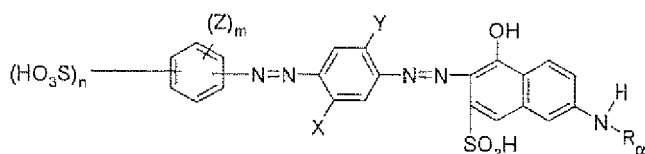
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The granulates in the formulations according to the invention may contain from 0 to 15 wt-% water (component c), based on the total weight of the granulate.

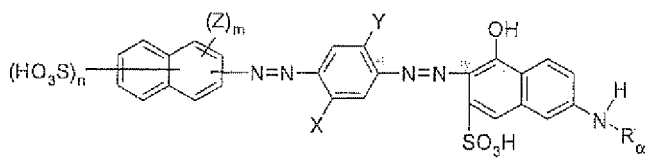
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The granulates in the formulations according to the invention preferably have an average particle size of < 500 µm. Greater preference is given to the particle size of the granulates being from 40 to 400 µm.

- 5 A preferred embodiment of the present invention relates to granulates comprising
- a) from 2 to 75 wt-% of at least one composition comprising
- at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and
- at least one azo dyestuff of formulae



or



wherein

X and Y, independently of one another, are each hydrogen;

C₁-C₄-alkyl or C₁-C₄-alkoxy,

R_α is hydrogen or aryl,

Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the granulate,

- b) from 10 to 95 wt-% of at least one further additive selected from the group consisting of anionic or non-ionic dispersing agents; water-soluble organic polymers; inorganic salt; low-molecular-weight organic acid or a salt thereof; wetting agents; disintegrants such as, for example, powdered or fibrous cellulose, microcrystalline cellulose; fillers
- 20
- 25

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such as, for example, dextrin; water-insoluble or water-soluble dyes or pigments; dissolution accelerators; optical brighteners; aluminium silicates; talc, kaolin, TiO_2 , SiO_2 and magnesium trisilicate, and

5 c) from 0 to 15 wt-% water, based on the total weight of the granulate.

A more preferred embodiment of the present invention relates to granulates comprising

a) from 2 to 75 wt-% of at least one composition comprising
 at least one phthalocyanine compound of formula (1a), (1b),
 10 (2a), (3), (4), (4a), (5), (6) and/or (7), and
 at least one azo dyestuff of formula (A), (B), and/or (C) and/or
 at least one triphenylmethane dyestuff of formula (D), (E), (F),
 (G), (H) and/or (I) as defined above, based on the total weight
 of the granulate,

15 b) from 10 to 95 wt-% of at least one further additive selected from the group consisting
 of anionic or non-ionic dispersing agents; water-soluble organic
 polymers; inorganic salt; low-molecular-weight organic acid or a
 salt thereof; wetting agents; disintegrants such as, for example,
 powdered or fibrous cellulose, microcrystalline cellulose; fillers
 20 such as, for example, dextrin; water-insoluble or water-soluble
 dyes or pigments; dissolution accelerators; optical brighteners;
 aluminium silicates; talc, kaolin, TiO_2 , SiO_2 and magnesium
 trisilicate, and

c) from 0 to 15 wt-% water, based on the total weight of the granulate.

25

A further embodiment is a liquid formulation comprising a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff.

30 Preferably a liquid formulation comprising

(a) 0.01 – 95 wt-%, preferably 1 – 80 wt-%, more preferably 5 – 70 wt-% of a composition comprising at least one water-soluble phthalocyanine compound and at least one azo dyestuff and/or at least one triphenylmethane dyestuff as defined above, based on the total weight of the liquid formulation,

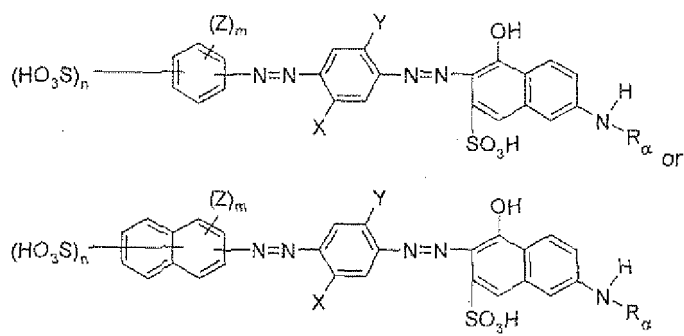
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- (b) 5 – 99.99 wt-%, preferably 20 – 99 wt-%, more preferably 30 – 95 wt-%, based on the total weight of the liquid formulation, of at least one organic solvent and
- (c) 0 – 10 wt-%, preferably 0 – 5 wt-%, more preferably 0– 2 wt-%, based on the total weight of the liquid formulation, of at least one further additive.

5

More preferably a liquid formulation comprising

- (a) 0.01 – 95 wt-%, preferably 1 – 80 wt-%, more preferably 5 – 70 wt-% of a composition comprising at least one water-soluble phthalocyanine compound and at least one azo dyestuff formulae



10

wherein

X and Y , independently of one another, are each hydrogen;

$\text{C}_1\text{--C}_4\text{-alkyl}$ or $\text{C}_1\text{--C}_4\text{-alkoxy}$,

15

R_α is hydrogen or aryl,

Z is $\text{C}_1\text{--C}_4\text{-alkyl}$; $\text{C}_1\text{--C}_4\text{-alkoxy}$; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or at least one triphenylmethane dyestuff as defined above, based on the total weight of the liquid formulation,

20

- (b) 5 – 99.99 wt-%, preferably 20 – 99 wt-%, more preferably 30 – 95 wt-%, based on the total weight of the liquid formulation, of at least one organic solvent and
- (c) 0 – 10 wt-%, preferably 0 – 5 wt-%, more preferably 0– 2 wt-%, based on the total weight of the liquid formulation, of at least one further additive.

25

Especially preferred is a liquid formulation comprising

- (a) 0.01 – 95 wt-%, preferably 1 – 80 wt-%, more preferably 5 – 70 wt-% of at least one composition comprising

- 50 -

at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and

at least one azo dyestuff of formula (A), (B), and/or (C) and/or

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the liquid formulation,

5

(b) 5 – 99.99 wt-%, preferably 20 – 99 wt-%, more preferably 30 – 95 wt-%, based on the total weight of the liquid formulation, of at least one organic solvent and

(c) 0 – 10 wt-%, preferably 0 – 5 wt-%, more preferably 0- 2 wt-%, based on the total weight of the liquid formulation, of at least one further additive.

10

The preferences for the phthalocyanines, for the azo and triphenylmethane dyestuffs as defined above also apply for the liquid formulation.

As organic solvents, polar solvents are preferred. Especially preferred are C₁–C₄-alcohols or water.

15

If appropriate, the liquid formulation according to the invention can further comprise optional additives; examples are preservatives or mixtures of preservatives, such as chloroacetamide, triazine derivatives, benzoisothiazolines, 2-methyl-2H-isothiazol-3on, 2-octyl-2H-isothiazol-3on, 2-brom-2-nitropropan-1,3-diol or aqueous formaldehyde solution; Mg/Al silicates or mixtures of Mg/Al silicates, such as bentonite, montmorillonite, zeolites or highly disperse silicic acids; odour improvers and perfuming agent or mixtures thereof; antifoam agents or mixtures thereof; builders or mixtures thereof; protective colloids or mixtures thereof; stabilizers or mixtures thereof; sequestering agents and antifreeze agents or mixtures thereof, such as propylene glycol.

25

A preferred embodiment of the present invention related to a liquid formulation comprising

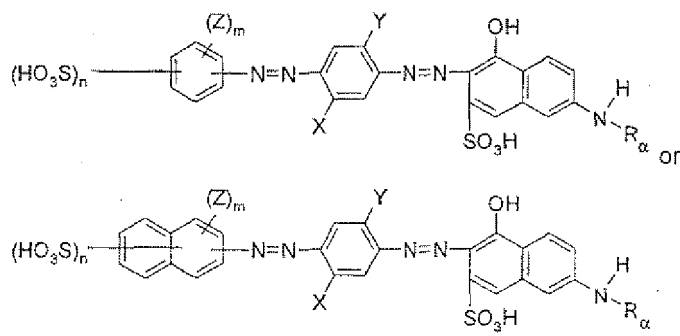
(a) 0.01 – 95 wt-%, preferably 1 – 80 wt-%, more preferably 5 – 70 wt-% of at least one composition comprising

30

at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and

at least one azo dyestuff of formulae

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wherein

X and Y, independently of one another, are each hydrogen; C₁-C₄-alkyl or C₁-C₄-alkoxy,

R_α is hydrogen or aryl,

Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the liquid formulation,

(b) 5 – 99.99 wt-%, preferably 20 – 99 wt-%, more preferably 30 – 95 wt-%, based on the total weight of the liquid formulation, of C₁-C₄-alcohols or water, and

(c) 0 – 10 wt-%, preferably 0 – 5 wt-%, more preferably 0 – 2 wt-%, based on the total weight of the liquid formulation, of at least one additive selected from the group consisting of preservatives; Mg/Al silicates; odour improvers; perfuming agent; antifoam agents; builders; protective colloids; stabilizers; sequestering agents and antifreeze agents.

A more preferred embodiment of the present invention related to a liquid formulation comprising

(a) 0.01 – 95 wt-%, preferably 1 – 80 wt-%, more preferably 5 – 70 wt-% of at least one composition comprising

at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and

at least one azo dyestuff of formula (A), (B), and/or (C) and/or

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the liquid formulation,

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- (b) 5 – 99.99 wt-%, preferably 20 – 99 wt-%, more preferably 30 – 95 wt-%, based on the total weight of the liquid formulation, of C₁–C₄-alcohols or water, and
- (c) 0 – 10 wt-%, preferably 0 – 5 wt-%, more preferably 0– 2 wt-%, based on the total weight of the liquid formulation, of at least one additive selected from the group consisting of preservatives; Mg/Al silicates; odour improvers; perfuming agent; antifoam agents; builders; protective colloids; stabilizers; sequestering agents and antifreeze agents.

The composition according to the invention is used especially in a washing or softener formulation. Such a washing or softener formulation may be in solid, liquid, gel-like or paste-like form, for example in the form of a liquid, non-aqueous washing agent composition containing not more than 5 wt-%, preferably from 0 to 1 wt-%, water and based on a suspension of a builder substance in a non-ionic surfactant, for example as described in GB-A-2 158 454.

- The washing formulations may also be in the form of powders or (super-)compact powders, in the form of single- or multi-layer tablets (tabs), in the form of washing agent bars, washing agent blocks, washing agent sheets, washing agent pastes or washing agent gels, or in the form of powders, pastes, gels or liquids used in capsules or in pouches (sachets).
- However, the washing agent compositions are preferably in the form of non-aqueous formulations, powders, tabs or granules.

The present invention accordingly relates also to washing agent formulations containing

- I) from 5 to 70 wt-% A) of at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing agent formulation,
- II) from 5 to 60 wt-% C) of at least one builder substance, based on the total weight of the washing agent formulation,
- III) from 0 to 30 wt-% D) of at least one peroxide and, optionally, at least one activator, based on the total weight of the washing agent formulation, and
- IV) from 0.001 to 1 wt-% E) of at least one granulate which contains
- a) from 2 to 75 wt-% of at least one water-soluble phthalocyanine compound and at least one azo dyestuff and/or at least one

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- triphenylmethane dyestuff as defined above, based on the total weight of the granulate,
- b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the granulate, and
- 5 c) from 0 to 15 wt-% water, based on the total weight of the granulate, and
- V) from 0 to 60 wt-% F) of at least one further additive, and
- VI) from 0 to 5 wt-% G) water.

The sum of the wt-% of components I) – VI) in a formulation is always 100 %.

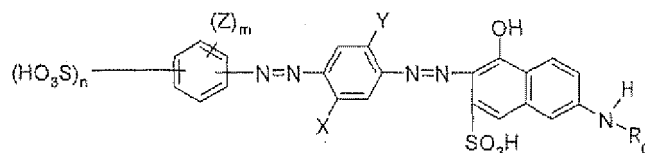
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All the preferences mentioned hereinbefore apply to the granulate E).

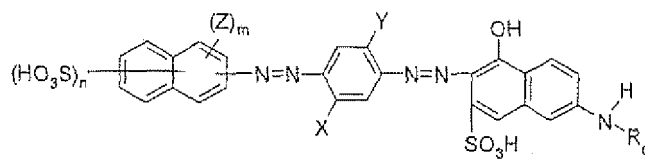
The present invention accordingly relates also to washing agent formulations containing

- I) from 5 to 70 wt-% A) of at least one anionic surfactant and/or B) at least
- 15 one non-ionic surfactant, based on the total weight of the washing agent formulation,
- II) from 5 to 60 wt-% C) of at least one builder substance, based on the total weight of the washing agent formulation,
- III) from 0 to 30 wt-% D) of at least one peroxide and, optionally, at least one
- 20 activator, based on the total weight of the washing agent formulation, and
- IV) from 0.001 to 1 wt-% E) of at least one granulate which contains
- a) from 2 to 75 wt-% of at least one water-soluble phthalocyanine compound and at least one azo dyestuff of formulae

25



or



wherein

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- 5 X and Y, independently of one another, are each hydrogen;
 C₁-C₄-alkyl or C₁-C₄-alkoxy,
 R_n is hydrogen or aryl,
 Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,
 n is 1 or 2 and
 m is 0, 1 or 2, as well as the corresponding salts thereof and
 mixtures thereof and/or at least one triphenylmethane dyestuff
 as defined above, based on the total weight of the granulate,
 b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the
 10 granulate, and
 c) from 0 to 15 wt-% water, based on the total weight of the granulate, and
 V) from 0 to 60 wt-% F) of at least one further additive, and
 VI) from 0 to 5 wt-% G) water.

- 15 The percentages of components I) to VI) in the washing agent formulations herein below
 are in all cases based on the total weight of the washing agent formulation.

The anionic surfactant A) can be, for example, a sulfate, sulfonate or carboxylate surfactant
 or a mixture thereof. Preferred sulfates are those having from 12 to 22 carbon atoms in the
 20 alkyl radical, optionally in combination with alkyl ethoxysulfates in which the alkyl radical
 has from 10 to 20 carbon atoms.

Preferred sulfonates are e.g. alkylbenzenesulfonates having from 9 to 15 carbon atoms in
 the alkyl radical. The cation in the case of anionic surfactants is preferably an alkali metal
 25 cation, especially sodium.

The anionic surfactant component may be, e.g., an alkylbenzenesulfonate, an
 alkylsulfate, an alkylethersulfate, an olefinsulfonate, an alkanesulfonate, a fatty
 acid salt, an alkyl or alkenyl ether carboxylate or an α -sulfofatty acid salt or an
 30 ester thereof. Preferred are alkylbenzenesulfonates having 10 to 20 carbon atoms
 in the alkyl group, alkylsulfates having 8 to 18 carbon atoms, alkylethersulfates
 having 8 to 22 carbon atoms, and fatty acid salts being derived from palm oil or
 tallow and having 8 to 22 carbon atoms. The average molar number of ethylene
 oxide added in the alkylethersulfate is preferably 1 to 22, preferably 1 to 10. The

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salts are preferably derived from an alkaline metal like sodium and potassium, especially sodium. Highly preferred carboxylates are alkali metal sarcosinates of formula

R-CO(R₁)CH₂COOM₁ in which R is alkyl or alkenyl having 8-20 carbon atoms in
 5 the alkyl or alkenyl radical, R₁ is C₁-C₄ alkyl and M₁ is an alkali metal, especially sodium.

The nonionic surfactant component may be, e.g., primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of
 10 from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

15

The total amount of anionic surfactant and nonionic surfactant is preferably 5-50 wt-%, preferably 5-40 wt-% and more preferably 5-30 wt-%. As to these surfactants it is preferred that the lower limit is 10 wt-%.

Preferred carboxylates are alkali metal sarcosinates of formula R₁₉-CO-N(R₂₀)-CH₂COOM¹
 20 wherein R₁₉ is alkyl or alkenyl having from 8 to 20 carbon atoms in the alkyl or alkenyl radical, R₂₀ is C₁-C₄alkyl and M¹ is an alkali metal.

The non-ionic surfactant B) can be, for example, a condensation product of from 3 to 8 mol
 25 of ethylene oxide with 1 mol of a primary alcohol having from 9 to 15 carbon atoms.

25

As builder substance C) there come into consideration, for example, alkali metal phosphates, especially tripolyphosphates, carbonates or hydrogen carbonates, especially their sodium salts, silicates, aluminosilicates, polycarboxylates, polycarboxylic acids, organic phosphonates, aminoalkylenepoly(alkylenephosphonates) or mixtures of those compounds.

30

Especially suitable silicates are sodium salts of crystalline layered silicates of the formula NaHSi_tO_{2t+1}.pH₂O or Na₂Si_tO_{2t+1}.pH₂O wherein t is a number from 1.9 to 4 and p is a number from 0 to 20.

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Among the aluminosilicates, preference is given to those commercially available under the names zeolithe A, B, X and HS, and also to mixtures comprising two or more of those components. Zeolithe A is preferred.

- 5 Among the polycarboxylates, preference is given to polyhydroxycarboxylates, especially citrates, and acrylates and also copolymers thereof with maleic anhydride. Preferred polycarboxylic acids are nitrilotriacetic acid, ethylenediaminetetraacetic acid and ethylenediamine disuccinate either in racemic form or in the enantiomerically pure (S,S) form.
- 10 Phosphonates or aminoalkylenepoly(alkylenephosphonates) that are especially suitable are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylenephosphonic acid), ethylenediaminetetramethylenephosphonic acid, hexamethylenediamin N,N,N',N' tetrakis methanphosphonic acid and diethylenetriaminepentamethylenephosphonic acid, as well as the salts therefrom.
- 15 Suitable peroxide components include, for example, the organic and inorganic peroxides (like sodium peroxides) known in the literature and available commercially that bleach textile materials at conventional washing temperatures, for example at from 5 to 95°C.
- 20 In particular, the organic peroxides are, for example, monoperoxides or polyperoxides having alkyl chains of at least 3, preferably 6 to 20, carbon atoms; in particular diperoxydicarboxylates having 6 to 12 C atoms, such as diperoxyperacetates, diperoxypersebacates, diperoxyphthalates and/or diperoxydodecanedioates, especially their corresponding free acids, are of
- 25 interest.
- Especially preferred are mono- oder polyperoxide, especially organic peracids or their salts such as phthalimidoperoxycapronic acid, peroxybenzoic acid, diperoxydodecandiacid, diperoxyonandiacid, diperoxydecandiacid, diperoxyphthalic acid or their salts.
- 30 The amount of peroxide is preferably 0.5-30 wt-%, preferably 1-20 wt-% and more preferably 1-15 wt-%. In case a peroxide is used, the lower limit is preferably 2 wt-%, especially 5 wt-%.

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Preferably, however, inorganic peroxides are used, for example persulfates, perborates, percarbonates and/or persulfates. It will be understood that mixtures of inorganic and/or organic peroxides can also be used. The peroxides may be in a variety of crystalline forms and have different water contents, and they may also be used together with other inorganic or organic compounds in order to improve their storage stability.

The peroxides are added to the agent preferably by mixing the components, for example using a screw metering system and/or a fluidised bed mixer.

10 The agents may comprise, in addition to the combination according to the invention, one or more optical brighteners, for example from the class bis-triazinylamino-stilbenedisulfonic acid, bis-triazolyl-stilbenedisulfonic acid, bis-styryl-biphenyl or bis-benzofuranyl-biphenyl, a bis-benzoxalyl derivative, bis-benzimidazolyl derivative or coumarin derivative or a pyrazoline derivative.

15 The detergents used will usually contain one or more auxiliaries such as soil suspending agents, for example sodium carboxymethylcellulose; salts for adjusting the pH, for example alkali or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and granulating properties, for example sodium sulphate; perfumes, and
20 also, if appropriate, antistatic and softening agents; such as smectite clays; photobleaching agents; pigments; and/or shading agents. These constituents should, of course, be stable to any bleaching system employed. Such auxiliaries can be present in an amount of, for example, 0.1 to 20 wt-%, preferably 0.5 to 10 wt-%, especially 0.5 to 5 wt-%, based on the total weight of the detergent.

25 Furthermore, the detergent can optionally contain enzymes. Enzymes can be added to detergents for stain removal. The enzymes usually improve the performance on stains that are either protein- or starch-based, such as those caused by blood, milk, grass or fruit juices. Preferred enzymes are cellulases, proteases, amylases and lipases. Preferred
30 enzymes are cellulases and proteases, especially proteases. Cellulases are enzymes which act on cellulose and its derivatives and hydrolyze them into glucose, cellobiose, celooligosaccharide. Cellulases remove dirt and have the effect of mitigating the roughness to the touch. Examples of enzymes to be used include, but are by no means limited to, the following:

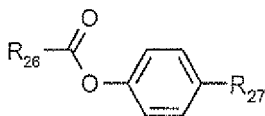
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proteases as given in US-B-6,242,405, column 14, lines 21 to 32;
 lipases as given in US-B-6,242,405, column 14, lines 33 to 46;
 amylases as given in US-B-6,242,405, column 14, lines 47 to 56; and
 cellulases as given in US-B-6,242,405, column 14, lines 57 to 64.

5

The enzymes can optionally be present in the detergent. When used, the enzymes are usually present in an amount of 0.01-5 wt-%, preferably 0.05-5 wt-% and more preferably 0.1-4 wt-%, based on the total weight of the detergent.

- 10 In addition to the bleach catalyst according to formula (1) it is also possible to use further transition metal salts or complexes known as bleach-activating active ingredients and/or conventional bleach activators, that is to say compounds that, under perhydrolysis conditions, yield unsubstituted or substituted perbenzo- and/or peroxy-carboxylic acids having from 1 to 10 carbon atoms, especially from 2 to 4 carbon atoms. Suitable bleach
- 15 activators include the customary bleach activators, mentioned at the beginning, that carry O- and/or N-acyl groups having the indicated number of carbon atoms and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylenediamine (TAED), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU), acylated triazine derivatives, especially
- 20 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), compounds of formula:



- wherein R_{26} is a sulfonate group, a carboxylic acid group or a carboxylate group, and wherein R_{27} is linear or branched (C_7 - C_{16})alkyl, especially activators known under the names SNOBS, SLOBS and DOBA, acylated polyhydric alcohols, especially triacetin, ethylene glycol
- 25 diacetate and 2,5-diacetoxy-2,5-dihydrofuran, and also acetylated sorbitol and mannitol and acylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), pentaacetylfructose, tetraacetylxylose and octaacetyllactose as well as acetylated, optionally N-alkylated glucamine and gluconolactone. It is also possible to use the combinations of conventional bleach activators known from German Patent Application
- 30 DE-A-44 43 177. Nitrile compounds that form perimine acids with peroxides also come into consideration as bleach activators.

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Further preferred additives to the agents according to the invention are dye fixing agents and/or polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor that have been released from the textiles under the washing conditions. Such polymers are preferably polyvinylpyrrolidones, polyvinylimidazole or polyvinylpyridine-
5 N-oxides which may have been modified by the incorporation of anionic or cationic substituents, especially those having a molecular weight in the range of from 5000 to 60000, more especially from 5000 to 50000. Such polymers are usually used in an amount of from 0.01 to 5 wt-%, preferably 0.05 to 5 wt-%, especially 0.1 to 2 wt-%, based on the total weight of the detergent. Preferred polymers are those given in WO-A-02/02865 (see
10 especially page 1, last paragraph and page 2, first paragraph).

A preferred washing agent formulation according to the invention consists of

- I) from 5 to 70 wt-% A) of at least one anionic surfactant from the group
15 consisting of alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical; alkyl-naphthalenesulfonates having from 6 to 16 carbon atoms in the alkyl radical in question; and alkali metal sarcosinates of the formula $R-CO-N(R_1)-CH_2COOM_1$, wherein R is alkyl or alkenyl having from 8 to 20 carbon atoms in the alkyl or alkenyl radical,
20 R_1 is C_1 - C_4 alkyl and M_1 is an alkali metal and/or
B) at least one non-ionic surfactant from the group consisting of condensation products of from 3 to
25 8 mols of ethylene oxide with 1 mol of primary alcohol containing from 9 to 20 carbon atoms,
II) from 5 to 60 wt-% C) of a builder substance from the group consisting of alkali metal phosphates; carbonates; hydrogen carbonates; silicates; aluminium silicates; polycarboxylates; poly-
30 carboxylic acids; organic phosphonates and amino-alkylenepoly(alkylenephosphonates), and
III) from 0 to 30 wt-% D) of a peroxide from the group consisting of organic mono- or poly-peroxides; organic peracids and salts

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thereof, persulfates; perborates; percarbonates and persilicates,

IV) from 0.001 to 1 wt-% E) of at least one granulate which contains

- 5 a) from 2 to 70 wt-% of at least one water-soluble phthalocyanine compound and at least one azo dyestuff and/or at least one triphenylmethane dyestuff as defined above, based on the total weight of the granulate,
- b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the granulate, and
- 10 c) from 0 to 15 wt-% water, based on the total weight of the granulate,
- V) from 0 to 60 % F) of further additives from the group consisting of optical brighteners; suspending agents for dirt; pH regulators; foam regulators; salts for regulating the spray-drying and granulating properties; fragrances; antistatic agents; fabric conditioners; enzymes; bleaching agents;
- 15 pigments; toning agents; polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor which have been released from the textiles under the washing conditions; and perborate activators, and
- VI) from 0 to 5 % G) water.

20

A more preferred washing agent formulation according to the invention consists of

- I) from 5 to 70 wt-% A) of at least one anionic surfactant from the group consisting of alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical; alkyl-naphthalenesulfonates having from 6 to 16 carbon atoms in the alkyl radical in question; and alkali metal sarcosinates of the formula $R-CO-N(R_1)-CH_2COOM_1$, wherein R is alkyl or alkenyl having from 8 to 20 carbon atoms in the alkyl or alkenyl radical,
- 25 R₁ is C₁-C₄alkyl and M₁ is an alkali metal and/or
- 30 B) at least one non-ionic surfactant from the group consisting of condensation products of from 3 to

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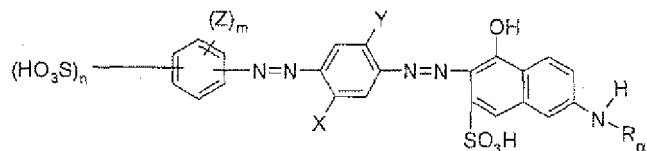
8 mols of ethylene oxide with 1 mol of primary alcohol containing from 9 to 20 carbon atoms,

II) from 5 to 60 wt-% C) of a builder substance from the group consisting of alkali metal phosphates; carbonates; hydrogen carbonates; silicates; aluminium silicates; polycarboxylates; polycarboxylic acids; organic phosphonates and amino-alkylenepoly(alkylenephosphonates), and

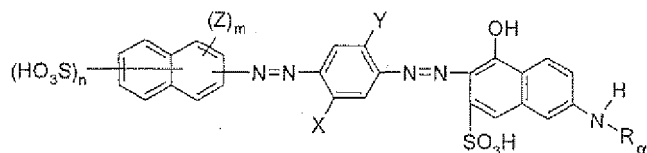
III) from 0 to 30 wt-% D) of a peroxide from the group consisting of organic mono- or poly-peroxides; organic peracids and salts thereof; persulfates; perborates; percarbonates and persilicates,

IV) from 0.001 to 1 wt-% E) of at least one granulate which contains

a) from 2 to 70 wt-% of at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and at least one azo dyestuff of formulae



or



wherein

X and Y, independently of one another, are each hydrogen;

C₁-C₄-alkyl or C₁-C₄-alkoxy,

R_α is hydrogen or aryl,

Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or

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- at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the granulate,
- b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the granulate, and
- 5 c) from 0 to 15 wt-% water, based on the total weight of the granulate,
- V) from 0 to 60 % F) of further additives from the group consisting of optical brighteners; suspending agents for dirt; pH regulators; foam regulators; salts for regulating the spray-drying and granulating properties; fragrances; antistatic agents; fabric conditioners; enzymes; bleaching agents; pigments; toning agents; polymers which, during the washing of
- 10 textiles, prevent staining caused by dyes in the washing liquor which have been released from the textiles under the washing conditions; and perborate activators, and
- 15 VI) from 0 to 5 % G) water.

An especially preferred washing agent formulation according to the invention consists of

- I) from 5 to 70 wt-% A) of at least one anionic surfactant from the group consisting of alkylbenzenesulfonates having from 9 to
- 20 15 carbon atoms in the alkyl radical; alkyl-naphthalenesulfonates having from 6 to 16 carbon atoms in the alkyl radical in question; and alkali metal sarcosinates of the formula $R-CO-N(R_1)-CH_2COOM_1$, wherein R is alkyl or alkenyl having from 8 to 20
- 25 carbon atoms in the alkyl or alkenyl radical, R_1 is C_1-C_4 alkyl and M_1 is an alkali metal and/or
- B) at least one non-ionic surfactant from the group consisting of condensation products of from 3 to
- 30 8 mols of ethylene oxide with 1 mol of primary alcohol containing from 9 to 20 carbon atoms,
- II) from 5 to 60 wt-% C) of a builder substance from the group consisting of alkali metal phosphates; carbonates; hydrogen carbonates; silicates; aluminium silicates; polycarboxylates; poly-

- carboxylic acids; organic phosphonates and amino-alkylenepoly(alkylenephosphonates), and
- III) from 0 to 30 wt-% D) of a peroxide from the group consisting of organic mono- or poly-peroxides; organic peracids and salts thereof; persulfates; perborates; percarbonates and persulfates,
- 5 IV) from 0.001 to 1 wt-% E) of at least one granulate which contains
- a) from 2 to 70 wt-% of at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and
- 10 at least one azo dyestuff of formula (A), (B), and/or (C) and/or
- at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the granulate,
- 15 b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the granulate, and
- c) from 0 to 15 wt-% water, based on the total weight of the granulate,
- V) from 0 to 60 % F) of further additives from the group consisting of optical brighteners; suspending agents for dirt; pH regulators; foam regulators; salts for
- 20 regulating the spray-drying and granulating properties; fragrances; antistatic agents; fabric conditioners; enzymes; bleaching agents; pigments; toning agents; polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor which have been released from the textiles under the washing
- 25 conditions; and perborate activators, and
- VI) from 0 to 5 % G) water.

The granulates E) are prepared according to known methods. Any known method is suitable to produce granules comprising the inventive mixture. Continuous or discontinuous methods

30 are suitable. Continuous methods, such as spray drying or fluidised bed granulation processes are preferred.

Especially suitable are spray-drying processes in which the active ingredient solution is sprayed into a chamber with circulating hot air. The atomisation of the solution is carried out

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using single or binary nozzles or is brought about by the spinning effect of a rapidly rotating disc. In order to increase the particle size, the spray-drying process may be combined with additional agglomeration of the liquid particles with solid nuclei in a fluidised bed that forms an integral part of the chamber (so-called fluidised spray). The fine particles (< 100 µm) obtained by a conventional spray-drying process may, if necessary after being separated from the exhaust gas flow, be fed as nuclei, without being further treated, directly into the spray cone of the atomiser of the spray-dryer, for the purpose of agglomeration with the liquid droplets of the active ingredient. During the granulation step, the water can be rapidly removed from the solutions comprising phthalocyanine compound, and, where appropriate, further additives, and it is expressly intended that agglomeration of the droplets forming in the spray cone, i.e. the agglomeration of droplets with solid particles, will take place. Preference is given to the use of agglomeration processes to produce the granulates according to the invention because such processes usually yield a higher bulk weight so that the granulates have better compatibility with washing agent formulations.

A further embodiment of the present invention comprises using, for preparation of the granulates, phthalocyanine solutions that have been purified by membrane separation procedures.

If necessary, the granules formed in the spray-dryer are removed in a continuous process, for example by a sieving operation. The fines and the oversize particles are either recycled directly to the process (without being redissolved) or are dissolved in the liquid active ingredient formulation and subsequently granulated again.

The granulates are resistant to abrasion, low in dust, free-flowing and can be readily metered. They are distinguished especially by very rapid solubility in water.

The granulates E) preferably have a density in the range from 500 to 900 g/l, dissolve rapidly in water and do not float on the surface of the washing agent solution. They may be added in the desired concentration of the phthalocyanine compound directly to the washing agent formulation.

The content of granulates E) in accordance with the invention in the formulations according to the invention is from 0.001 to 1 wt-%, preferably from 0.001 to 0.05 wt-% and very especially from 0.005 to 0.03 wt-%.

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The washing agent formulation according to the invention can be prepared in a generally known manner.

A formulation in powder form can be prepared, for example, by first preparing an initial powder by spray-drying an aqueous slurry comprising all of the afore-mentioned components except for components D) and E) and then adding the dry components D) and E) and mixing all of them together. It is also possible to start from an aqueous slurry which, although comprising components A) and C), does not comprise component B) or comprises only a portion of component B). The slurry is spray-dried; component E) is then mixed with component B) and added; and then component D) is mixed in dry. The components are preferably mixed with one another in such amounts that a solid compact washing agent composition in granule form is obtained, having a specific weight of at least 500 g/l.

In another preferred embodiment, the production of the washing agent composition is carried out in three steps. In the first step a mixture of anionic surfactant (and, where appropriate, a small amount of non-ionic surfactant) and builder substance is prepared. In the second step that mixture is sprayed with the major portion of the non-ionic surfactant and then, in the third step, peroxide and, where appropriate, catalyst, and the granulate according to the invention are added. That method is usually carried out in a fluidised bed. In a further preferred embodiment, the individual steps are not carried out completely separately, so that there is a certain amount of overlap between them. Such a method is usually carried out in an extruder, in order to obtain granulates in the form of "megapearls".

As an alternative thereto, the granulates according to the invention can, for the purpose of admixture with a washing agent in a post-dosing step, be mixed with other washing agent components such as phosphates, zeolites, brighteners or enzymes.

A mixture of that kind for post-dosing of the granulates is distinguished by a homogeneous distribution of the granulates according to the invention in the mixture and can consist of, for example, from 5 to 50 % granulates and from 95 to 50 % sodium tripolyphosphate. Where the dark appearance of the granulate in the washing agent composition is to be suppressed, this can be achieved, for example, by embedding the granules in droplets of a whitish meltable substance ("water-soluble wax") or, preferably, by encapsulating the granules in a melt consisting of, for example, a water-soluble wax, as described in EP-B-0 323 407 B1, a white solid (e.g. titanium dioxide) being added to the melt in order to reinforce the masking effect of the capsule.

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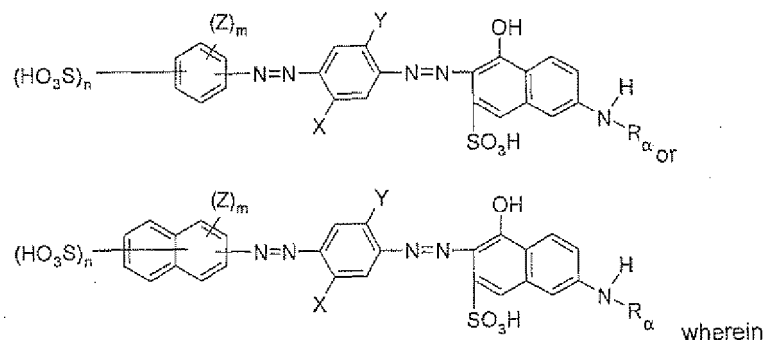
The detergent may also be formulated as an aqueous liquid comprising 5-50, preferably 10-35 wt-% of water or as a non-aqueous liquid detergent, containing not more than 5, preferably 0-1 wt-% of water. Non-aqueous liquid detergent compositions can contain other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5 wt-% to 90 wt-%, typically 10 wt-% to 50 wt-% of such carriers. The detergents can also be present as the so-called "unit liquid dose" form.

A further embodiment of the present invention is a fabric softener formulation comprising

- (a) at least one composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, which produces a relative hue angle of 220 – 320° and wherein the dyestuff is degraded when the composition is exposed to light,
- (b) at least one fabric softener.

A preferred embodiment of the present invention is a fabric softener formulation comprising

- (a) at least one composition comprising of at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and at least one azo dyestuff of formulae



- X and Y, independently of one another, are each hydrogen;
 C₁-C₄-alkyl or C₁-C₄-alkoxy,
 R_α is hydrogen or aryl,
 Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

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n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, which produces a relative hue angle of $220 - 320^\circ$ and wherein the dyestuff is degraded when the composition is exposed to light,

5

(b) at least one fabric softener.

An especially preferred embodiment of the present invention is a fabric softener formulation comprising

10

(a) at least one composition comprising of at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and at least one azo dyestuff of formula (A), (B), and/or (C) and/or at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, which produces a relative hue angle of $220 - 320^\circ$ and wherein the dyestuff is degraded when the composition is exposed to light,

15

(b) at least one fabric softener.

The preferences for the photocatalyst and the azo dyestuff as defined above also applies for the use in a fabric softener.

20

Fabric softeners, especially hydrocarbon fabric softeners, suitable for use herein are selected from the following classes of compounds:

(i) Cationic quaternary ammonium salts. The counter ion of such cationic quaternary ammonium salts may be a halide, such as chloride or bromide, methyl sulphate, or other ions well known in the literature. Preferably the counter ion is methyl sulfate or any alkyl sulfate or any halide, methyl sulfate being most preferred for the dryer-added articles of the invention.

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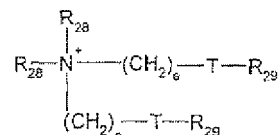
Examples of cationic quaternary ammonium salts include but are not limited to:

(1) Acyclic quaternary ammonium salts having at least two C_8 to C_{30} , preferably C_{12} to C_{22} alkyl or alkenyl chains, such as: ditallowdimethyl ammonium methylsulfate, di(hydrogenated tallow)dimethyl ammonium methylsulfate, di(hydrogenated tallow)dimethyl ammonium methylchloride, distearyldimethyl ammonium methyl-sulfate, dicocodimethyl ammonium methylsulfate and the like. It is especially preferred if the fabric softening compound is a

30

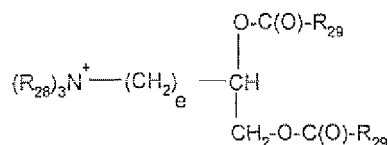
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water insoluble quaternary ammonium material which comprises a compound having two C₁₂ to C₁₈ alkyl or alkenyl groups connected to the molecule via at least one ester link. It is more preferred if the quaternary ammonium material has two ester links present. An especially preferred ester-linked quaternary ammonium material for use in the invention can be represented by the formula:



wherein each R₂₈ group is independently selected from C₁ to C₄ alkyl, hydroxyalkyl or C₂ to C₄ alkenyl groups; T is either -O-C(O)- or -C(O)-O-, and wherein each R₂₉ group is independently selected from C₈ to C₂₆ alkyl or alkenyl groups; and e is an integer from 0 to 5.

A second preferred type of quaternary ammonium material can be represented by the formula:



wherein R₁₄, e and R₁₅ are as defined above.

(2) Cyclic quaternary ammonium salts of the imidazolinium type such as di(hydrogenated tallow)dimethyl imidazolinium methylsulfate, 1-ethylene-bis(2-tallow-1-methyl) imidazolinium methylsulfate and the like;

(3) Diamido quaternary ammonium salts such as: methyl-bis(hydrogenated tallow amidoethyl)-2-hydroxyethyl ammonium methyl sulfate, methyl bi(tallowamidoethyl)-2-hydroxypropyl ammonium methylsulfate and the like;

(4) Biodegradable quaternary ammonium salts such as N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium methyl sulfate and N,N-di(tallowoyl-oxy-propyl)-N,N-dimethyl ammonium methyl sulfate. Biodegradable quaternary ammonium salts are described, for example, in U.S. Patents 4,137,180, 4,767,547 and 4,789,491 incorporated by reference herein.

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Preferred biodegradable quaternary ammonium salts include the biodegradable cationic diester compounds as described in U.S. Patent 4,137,180, herein incorporated by reference.

- (ii) Tertiary fatty amines having at least one and preferably two C₈ to C₃₀, preferably C₁₂ to C₂₂ alkyl chains. Examples include hardened tallow-di-methylamine and cyclic amines such as 1-(hydrogenated tallow)amidoethyl-2-(hydrogenated tallow) imidazoline. Cyclic amines, which may be employed for the compositions herein, are described in U.S. Patent 4,806,255 incorporated by reference herein.
- 5 (iii) Carboxylic acids having 8 to 30 carbon atoms and one carboxylic group per molecule. The alkyl portion has 8 to 30, preferably 12 to 22 carbon atoms. The alkyl portion may be linear or branched, saturated or unsaturated, with linear saturated alkyl preferred. Stearic acid is a preferred fatty acid for use in the composition herein. Examples of these carboxylic acids are commercial grades of stearic acid and palmitic acid, and mixtures thereof, which may contain small amounts of other acids.
- 10 (iv) Esters of polyhydric alcohols such as sorbitan esters or glycerol stearate. Sorbitan esters are the condensation products of sorbitol or iso-sorbitol with fatty acids such as stearic acid. Preferred sorbitan esters are monoalkyl. A common example of sorbitan ester is SPAN® 60 (ICI) which is a mixture of sorbitan and isosorbide stearates.
- 15 (v) Fatty alcohols, ethoxylated fatty alcohols, alkylphenols, ethoxylated alkylphenols, ethoxylated fatty amines, ethoxylated monoglycerides and ethoxylated diglycerides.
- 20 (vi) Mineral oils, and polyols such as polyethylene glycol.
- 25

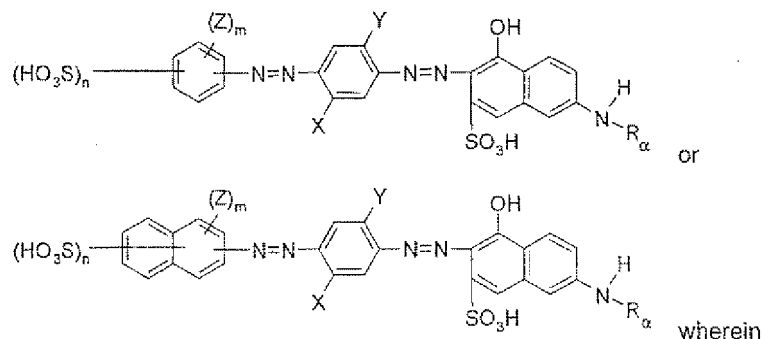
These softeners are more definitively described in U.S. Patent 4,134,838 the disclosure of which is incorporated by reference herein. Preferred fabric softeners for use herein are acyclic quaternary ammonium salts. Mixtures of the above mentioned fabric softeners may also be used.

30

The fabric softener formulation according to this invention comprises about 0.001 – 5 wt-%, preferably 0.001 – 3 wt-%, of at least one composition, which comprises at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and

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at least one azo dyestuff of formulae



X and Y, independently of one another, are each hydrogen;

5 C₁-C₄-alkyl or C₁-C₄-alkoxy,

R_α is hydrogen or aryl,

Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or

10 at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the fabric softener formulation

A preferred fabric softener formulation according to this invention comprises about 0.001 – 5 wt-%, preferably 0.001 – 3 wt-%, of at least one composition, which comprises at least one

15 phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and

at least one azo dyestuff of formula (A), (B), and/or (C) and/or

at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, based on the total weight of the fabric softener formulation.

20 The fabric softener formulation employed in the present invention preferably contains about 0.1 to about 95 wt-%, based on the total weight of the fabric softening composition, of the fabric softener formulation. Preferred is an amount of 0.5 to 50 wt-%, especially an amount of 2 to 50 wt-% and most preferably an amount of 2 to 30 wt-%.

25 The fabric softening composition may also comprise additives which are customary for standard commercial fabric softening compositions, for example alcohols, such as ethanol, n-propanol, i-propanol, polyhydric alcohols, for example glycerol and propylene glycol; amphoteric and nonionic surfactants, for example carboxyl derivatives of imidazole,

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oxyethylated fatty alcohols, hydrogenated and ethoxylated castor oil, alkyl polyglycosides, for example decyl polyglucose and dodecylpolyglucose, fatty alcohols, fatty acid esters, fatty acids, ethoxylated fatty acid glycerides or fatty acid partial glycerides; also inorganic or organic salts, for example water-soluble potassium, sodium or magnesium salts, non-
 5 aqueous solvents, pH buffers, perfumes, dyes, hydrotropic agents, antifoams, anti redeposition agents, enzymes, optical brighteners, antishrink agents, stain removers, germicides, fungicides, dye fixing agents or dye transfer inhibitors (as described in WO-A-02/02865), antioxidants, corrosion inhibitors, wrinkle recovery or wet soiling reduction agent, such as polyorganosiloxanes. The latter two additives are described in WO0125385.

10

Such additives are preferably used in an amount of 0 to 30 wt-%, based on the total weight of the fabric softening composition. Preferred is an amount of 0 to 20 wt-%, especially an amount of 0 to 10 wt-% and most preferably an amount of 0 to 5 wt-%, based on the total weight of the fabric softening composition.

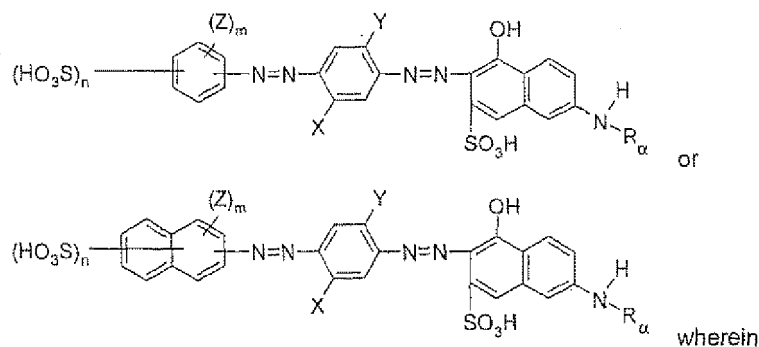
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The fabric softener compositions are preferably in liquid aqueous form. The fabric softener compositions preferably contain a water content of 25 to 90 wt-%, based on the total weight of the composition. More preferably the water content is 50 to 90 wt-%, especially 60 to 90 wt-%.

20

A preferred embodiment of the present invention is a fabric softener formulation comprising
 (a) 0.001 – 5wt-% at least on composition comprising of at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and
 at least one azo dyestuff of formulae

25



X and Y, independently of one another, are each hydrogen;
 C₁-C₄-alkyl or C₁-C₄-alkoxy,

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R_α is hydrogen or aryl,

Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof and/or

- 5 at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, which produces a relative hue angle of 220 – 320° and wherein the dyestuff is degraded when the composition is exposed to light,

- (b) 0.1 – 95 wt-% of at least one fabric softener selected from the above defined classes (i) – (vi),

- 10 (c) 0 – 30 wt-% of at least one additive selected from the group consisting of alcohols; amphoteric and nonionic surfactants; inorganic or organic salts; non-aqueous solvents; pH buffers; perfumes, dyes; hydrotropic agents; antifoams, anti redeposition agents; enzymes; optical brighteners; antishrink agents; stain removers; germicides; fungicides; dye fixing agents or dye transfer inhibitors; antioxidants; corrosion

15 inhibitors; wrinkle recovery or wet soiling reduction agent, and

- (d) 25 – 90 wt-% of water.

A more preferred embodiment of the present invention is a fabric softener formulation comprising

- 20 (a) 0.001 – 5wt-% at least on composition comprising of at least one phthalocyanine compound of formula (1a), (1b), (2a), (3), (4), (4a), (5), (6) and/or (7), and at least one azo dyestuff of formula (A), (B), and/or (C) and/or at least one triphenylmethane dyestuff of formula (D), (E), (F), (G), (H) and/or (I) as defined above, which produces a relative hue angle of 220 – 320° and wherein the

25 dyestuff is degraded when the composition is exposed to light,

- (b) 0.1 – 95 wt-% of at least one fabric softener selected from the above defined classes (i) – (vi),

- (c) 0 – 30 wt-% of at least one additive selected from the group consisting of alcohols; amphoteric and nonionic surfactants; inorganic or organic salts; non-aqueous solvents; pH buffers; perfumes, dyes; hydrotropic agents; antifoams, anti redeposition agents; enzymes; optical brighteners; antishrink agents; stain removers; germicides; fungicides; dye fixing agents or dye transfer inhibitors; antioxidants; corrosion

30 inhibitors; wrinkle recovery or wet soiling reduction agent, and

- (d) 25 – 90 wt-% of water.

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The fabric softener compositions preferably have a pH value from 2.0 to 9.0, especially 2.0 to 5.0.

The fabric softener compositions can, for example, be prepared as follows:

- 5 Firstly, an aqueous formulation of the cationic polymer is prepared as described above. The fabric softener composition according to the invention is usually, but not exclusively, prepared by firstly stirring the active substance, i.e. the hydrocarbon based fabric softening component, in the molten state into water, then, where required, adding further desired additives and, finally, adding the formulation of the cationic polymer. The fabric softener
10 composition can, for example, also be prepared by mixing a preformulated fabric softener with the cationic polymer.

These fabric softener compositions are traditionally prepared as dispersions containing for example up to 30 wt-% of active material in water. They usually have a turbid appearance.

- 15 However, alternative formulations usually containing actives at levels of 5 to 40 wt-% along with solvents can be prepared as microemulsions, which have a clear appearance (as to the solvents and the formulations see for example US-A-5,543,067 und WO-A-98/17757).

- Examples of suitable textile fibre materials which can be treated with the liquid rinse
20 conditioner composition are materials made of silk, wool, polyamide, acrylics or polyurethanes, and, in particular, cellulosic fibre materials and blends of all types. Such fibre materials are, for example, natural cellulose fibres, such as cotton, linen, jute and hemp, and regenerated cellulose. Preference is given to textile fibre materials made of cotton. The fabric softener compositions are also suitable for hydroxyl-containing fibres which are present in
25 mixed fabrics, for example mixtures of cotton with polyester fibres or polyamide fibres. The following Examples serve to illustrate the invention without the invention being limited thereto. Parts and percentages are by weight unless specified otherwise. Temperature is given in degree Celsius unless specified otherwise.

30 **Examples**

Degradation Experiments

The aqueous mixture of the photocatalyst and the dyestuff or the components alone were exposed in the given concentration in a closed 250ml glass bottle, containing 125 ml of the

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mixture to sunlight. The intensity measured with a Roline RO-1322 Digital Lux meter in front of the bottles was within the range of 4500-6000 Lux.

The degradation of the components was determined from spectrophotometric data gained with a HP 8452 Diode array spectrophotometer. The absorption of the mixtures was

5 measured at the respective absorption maximum of the components.

(Photocatalyst 670nm, Dyestuff 550nm). While there is only a small overlap of the two absorption spectrum at the maximum absorption of the photocatalyst at 670nm, there may be an appreciable overlap at the absorption maximum of the dyestuff. The absorption was determined at the start and then every 2 hours. The loss after two hours is given in

10 percentage of the initial concentration and is corrected where the overlap is considerable.

The used photocatalysts are

Photocatalyst 1: mixture of sulfonated Al- and Zn tetrabenzotetraaza-Porphyrines (Tinolux® BMC liq)

15 Photocatalyst 2: sulfonated Zn tetrabenzotetraaza-Porphyrine

The used dyestuffs are those of formula (A) and (B) as defined on epage 13.

The results are summarized in Table 1.

Table 1

	Photo-catalyst	Concentration Photocatalyst [μmol/l]	Dyestuff	Concentration Dyestuff [μmol/l]	Degradation of the Photocatalyst after 2 hours	Degradation of the Dyestuff after 2 hours
1	1	3.6			11.69%	
2	1	3.6	B	1.44	10.75%	4.65%
3	1	3.6	B	3.25	9.74%	5.36%
4	1	3.6	B	5.57	10.01%	4.58%
5	1	3.6	B	6.49	11.01%	5.50%
6	1	3.6	B	30.30	8.61%	3.63%
7	1	18	B	7.21	6.43%	6.72%
8	-----	-----	B	4.33	---	0.20%
9	2	3			17.19%	
10	2	3	B	4.33	15.71%	5.72%
11	2	3	A	4.41	9.51%	20.50%
12	----	----	A	4.41	---	0.20%
13	1	3.6	A	2.94	7.42%	17.18%
14	1	3.6	A	6.62	5.38%	16.13%
15	1	3.6	A	11.35	4.62%	15.02%

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	Photo-catalyst	Concentration Photocatalyst [$\mu\text{mol/l}$]	Dyestuff	Concentration Dyestuff [$\mu\text{mol/l}$]	Degradation of the Photocatalyst after 2 hours	Degradation of the Dyestuff after 2 hours
16	1	3.6	A	13.24	4.57%	15.47%
17	1	18	A	14.71	5.66%	20.51%

Determination of Hue angle

- The hue angle was determined from the experimental spectra of the starting mixture collected in the transmission mode, using the ordinary calculation modulus for the chosen light source (D 65 or A) and 10° observer. The mixtures are prepared in analogy to the Degradation Examples 1 – 17.

The results are summarized in Table 2

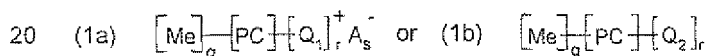
Table 2

	Photo-catalyst	Concentration Photocatalyst [$\mu\text{mol/l}$]	Dyestuff	Concentration Dyestuff [$\mu\text{mol/l}$]	Hue Angle D 65	Hue Angle Light A
18	1	3.6	---	---	201.17	207.00
19	1	3.6	2	1.44	223.68	222.52
20	1	3.6	2	3.25	248.89	240.14
21	1	3.6	2	5.57	269.50	257.22
22	1	3.6	2	6.49	276.34	263.29
23	1	3.6	2	30.30	307.23	299.40
24	2	3	---	---	---	---
25	2	3	2	4.33	---	---
26	2	3	1	4.41	---	---
27	1	3.6	1	2.94	256.37	244.51
28	1	3.6	1	6.62	287.85	275.13
29	1	3.6	1	11.35	300.69	291.83
30	1	3.6	1	13.24	303.50	295.70
31	1	3.6	1	61.786	317.24	315.78

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CLAIMS

1. A composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, which produce a relative hue angle of 220 –
 5 320° and wherein the dyestuff component is degraded when the composition is exposed to light.
2. A composition according to Claim 1 wherein the dyestuff component is degraded when the composition is exposed to sunlight.
- 10 3. A composition according to Claim 1 or 2 wherein the decrease rate of the azo dyestuff(s) and/or the triphenylmethane dyestuff(s) is at least 1 % per 2 hours.
4. A composition according to Claim 1, 2 or 3 wherein the photocatalyst is a water-soluble phthalocyanine of Zn, Fe(II), Ca, Mg, Na, K, Al, Si(IV), P(V), Ti(IV), Ge(IV), Cr(VI), Ga(III),
 15 Zr(IV), In(III), Sn(IV) or Hf(VI).
5. A composition according to Claim 1, 2, 3 or 4 wherein the photocatalyst is a water-soluble phthalocyanine of the formula



in which

PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Zr; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV);
 In(III); Sn(IV) or Hf(VI);

25 Z_1 is a halide; sulfate; nitrate; carboxylate; alkanolate; or hydroxyl ion;

q is 0; 1 or 2;

r is 1 to 4;

Q_1 is a sulfo or carboxyl group; or a radical of the formula
 $-\text{SO}_2\text{X}_2-\text{R}_1-\text{X}_3^+$; $-\text{O}-\text{R}_1-\text{X}_3^+$; or $-(\text{CH}_2)_t-\text{Y}_1^+$;

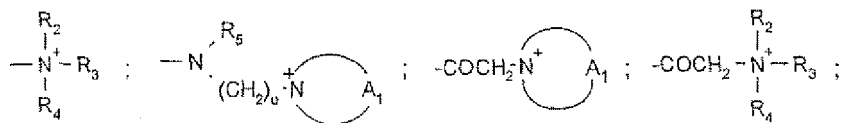
30 in which

R_1 is a branched or unbranched C_4 - C_6 alkylene; or 1,3- or 1,4-phenylene;

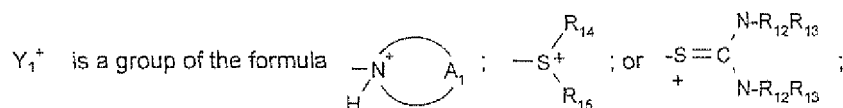
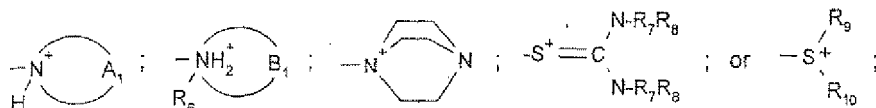
X_2 is $-\text{NH}-$; or $-\text{N}-\text{C}_1-\text{C}_5$ alkyl;

X_3^+ is a group of the formula

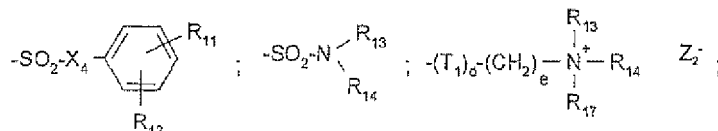
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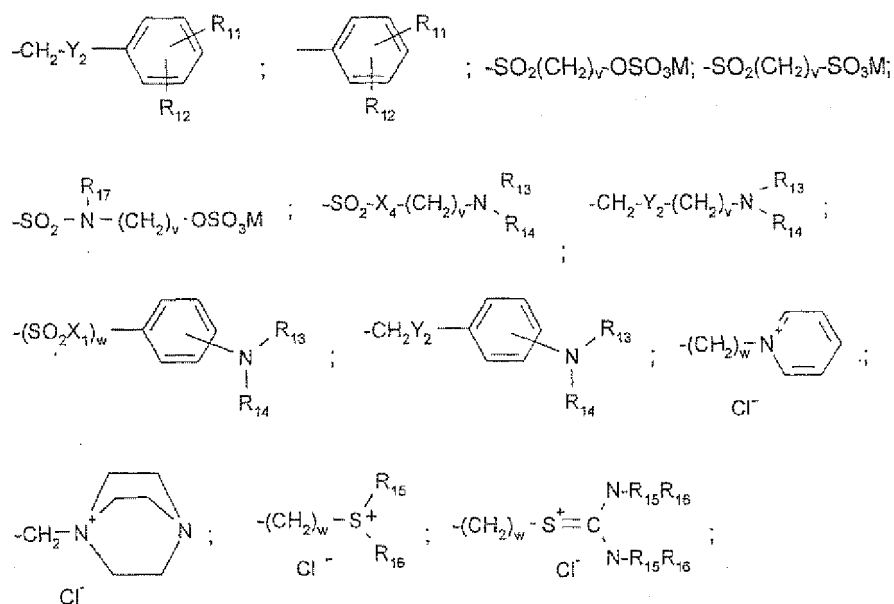
or, in the case where $R_1 = C_1\text{-}C_6\text{alkylene}$, also a group of the formula



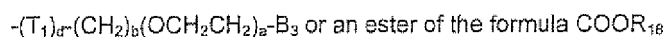
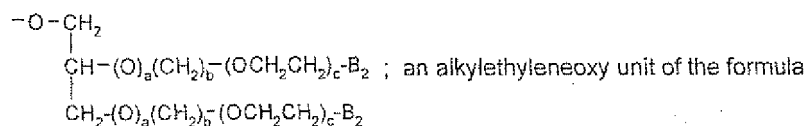
- 5 t is 0 or 1;
 where in the above formulae
 R_2 and R_3 independently of one another are $C_1\text{-}C_6\text{alkyl}$;
 R_4 is $C_1\text{-}C_6\text{alkyl}$; $C_5\text{-}C_7\text{cycloalkyl}$ or NR_7R_8 ;
 R_5 and R_6 independently of one another are $C_1\text{-}C_6\text{alkyl}$;
 10 R_7 and R_8 independently of one another are hydrogen or $C_1\text{-}C_6\text{alkyl}$;
 R_9 and R_{10} independently of one another are unsubstituted $C_1\text{-}C_6\text{alkyl}$ or $C_1\text{-}C_6\text{alkyl}$
 substituted by hydroxyl, cyano, carboxyl, carb- $C_1\text{-}C_6\text{alkoxy}$, $C_1\text{-}C_6\text{alkoxy}$, phenyl,
 naphthyl or pyridyl;
 u is from 1 to 6;
 15 A_1 is a unit which completes an aromatic 5- to 7-membered nitrogen heterocycle, which
 may where appropriate also contain one or two further nitrogen atoms as ring
 members, and
 B_1 is a unit which completes a saturated 5- to 7-membered nitrogen heterocycle, which
 may where appropriate also contain 1 to 2 nitrogen, oxygen and/or sulfur atoms as ring
 20 members;
 Q_2 is hydroxyl; $C_1\text{-}C_{22}\text{alkyl}$; branched $C_3\text{-}C_{22}\text{alkyl}$; $C_2\text{-}C_{22}\text{alkenyl}$; branched $C_3\text{-}C_{22}\text{alkenyl}$
 and mixtures thereof; $C_1\text{-}C_{22}\text{alkoxy}$; a sulfo or carboxyl radical; a radical of the formula



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- 5 a branched alkoxy radical of the formula
- $$\begin{array}{c}
 \text{CH}_2-(\text{O})_a(\text{CH}_2)_b-(\text{OCH}_2\text{CH}_2)_c-\text{B}_2 \\
 | \\
 \text{---O---CH} \\
 | \\
 \text{CH}_2-(\text{O})_a(\text{CH}_2)_b-(\text{OCH}_2\text{CH}_2)_c-\text{B}_2
 \end{array}$$



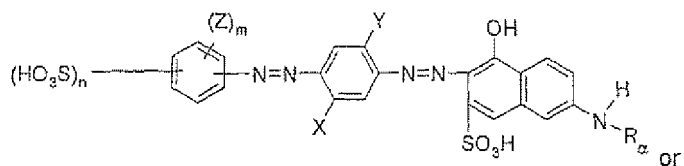
in which

- B_2 is hydrogen; hydroxyl; C_1 - C_{30} alkyl; C_1 - C_{30} alkoxy; $-\text{CO}_2\text{H}$; $-\text{CH}_2\text{COOH}$; $-\text{SO}_3^-\text{M}_1$;
 10 $-\text{OSO}_3^-\text{M}_1$; $-\text{PO}_3^{2-}\text{M}_1$; $-\text{OPO}_3^{2-}\text{M}_1$; and mixtures thereof;
 B_3 is hydrogen; hydroxyl; $-\text{COOH}$; $-\text{SO}_3^-\text{M}_1$; $-\text{OSO}_3^-\text{M}_1$ or C_1 - C_8 alkoxy;
 M_1 is a water-soluble cation;
 T_1 is $-\text{O}-$ or $-\text{NH}-$;
 X_1 and X_4 independently of one another are $-\text{O}-$; $-\text{NH}-$ or $-\text{N}-\text{C}_1-\text{C}_5$ alkyl;
 15 R_{11} and R_{12} independently of one another are hydrogen; a sulfo group and salts thereof; a carboxyl group and salts thereof or a hydroxyl group; at least one of the radicals R_{11} and R_{12} being a sulfo or carboxyl group or salts thereof;
 Y_2 is $-\text{O}-$; $-\text{S}-$; $-\text{NH}-$ or $-\text{N}-\text{C}_1-\text{C}_5$ alkyl;

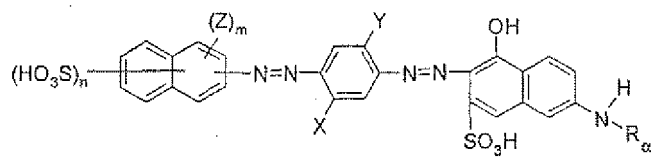
- 79 -

- R_{13} and R_{14} independently of one another are hydrogen; C_1 - C_6 alkyl; hydroxy- C_1 - C_6 alkyl; cyano- C_1 - C_6 alkyl; sulfo- C_1 - C_6 alkyl; carboxy or halogen- C_1 - C_6 alkyl; unsubstituted phenyl or phenyl substituted by halogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy; sulfo or carboxyl or R_{13} and R_{14} together with the nitrogen atom to which they are bonded form a saturated
- 5 5- or 6-membered heterocyclic ring which may additionally also contain a nitrogen or oxygen atom as a ring member;
- R_{15} and R_{16} independently of one another are C_1 - C_6 alkyl or aryl- C_1 - C_6 alkyl radicals;
- R_{17} is hydrogen; an unsubstituted C_1 - C_6 alkyl or C_1 - C_6 alkyl substituted by halogen, hydroxyl, cyano, phenyl, carboxyl, carb- C_1 - C_6 alkoxy or C_1 - C_6 alkoxy;
- 10 R_{18} is C_1 - C_{22} alkyl; branched C_3 - C_{22} alkyl; C_1 - C_{22} alkenyl or branched C_3 - C_{22} alkenyl; C_3 - C_{22} glycol; C_1 - C_{22} alkoxy; branched C_3 - C_{22} alkoxy; and mixtures thereof;
- M is hydrogen; or an alkali metal ion or ammonium ion,
- Z_2^- is a chlorine; bromine; alkylsulfate or aralkylsulfate ion;
- a is 0 or 1;
- 15 b is from 0 to 6;
- c is from 0 to 100;
- d is 0; or 1;
- e is from 0 to 22;
- v is an integer from 2 to 12;
- 20 w is 0 or 1; and
- A^- is an organic or inorganic anion, and
- s is equal to r in cases of monovalent anions A^- and is $\leq r$ in cases of polyvalent anions, it being necessary for A_s^- to compensate the positive charge; where, when $r \neq 1$, the radicals Q_1 can be identical or different,
- 25 and where the phthalocyanine ring system may also comprise further solubilising groups.

6. A composition according to any one of the preceeding claims wherein the azo dyestuff is a compound of formulae



- 80 -



wherein

X and Y, independently of one another, are each hydrogen; C₁-C₄-alkyl or C₁-C₄-alkoxy,

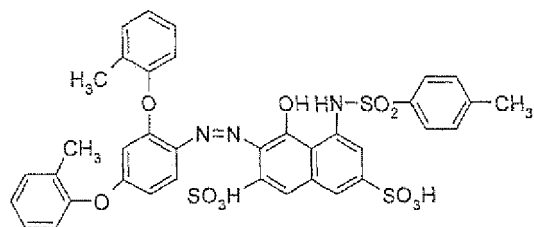
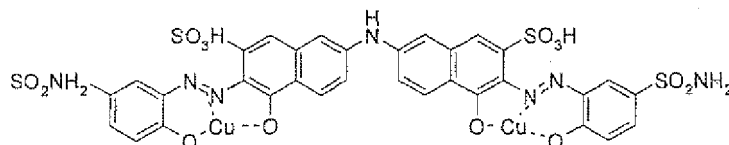
R_α is hydrogen or aryl,

5 Z is C₁-C₄-alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl,

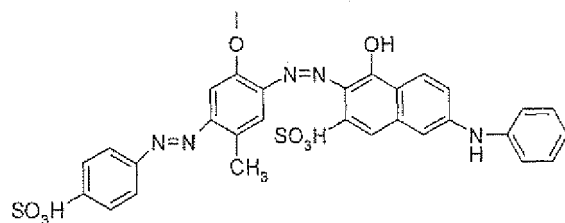
n is 1 or 2 and

m is 0, 1 or 2, as well as the corresponding salts thereof and mixtures thereof.

7. A composition according to any one of the preceding claims wherein the azo dyestuff
10 is a compound of formula

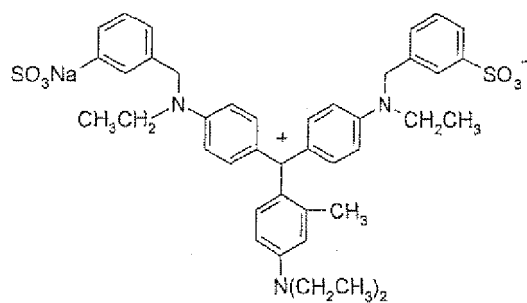
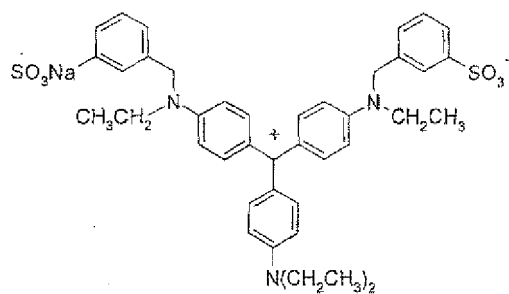
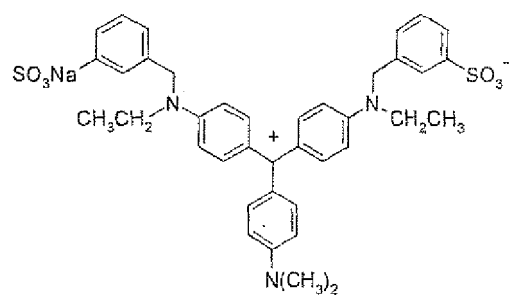


and/or

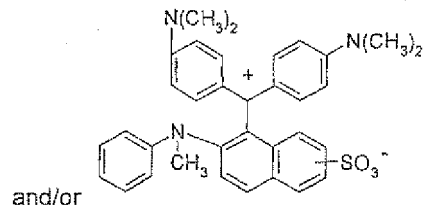
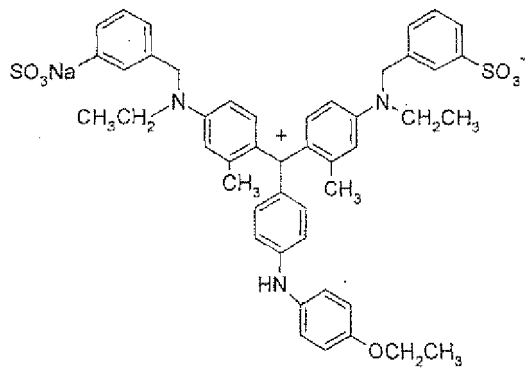
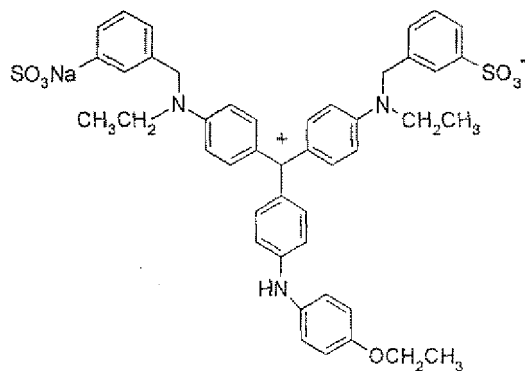


15 8. A composition according to any one of the preceding claims wherein the triphenylmethane dyestuff is a compound of formula

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9. A composition according to any one of the preceeding claims wherein at least one
5 FWA is comprised.
10. A granular formulation comprising a composition according to claims 1 - 9.
11. A granular formulation according to claim 9 comprising
- | | | |
|----|-----------------------|--|
| 10 | a) from 2 to 75 wt-% | of at least one water-soluble phthalocyanine compound and at least one azo dyestuff and/or at least one triphenylmethane dyestuff as defined in claim 1 - 9, based on the total weight of the granulate, |
| 15 | b) from 10 to 95 wt-% | of at least one further additive, based on the total weight of the granulate, and |
| | c) from 0 to 15 wt-% | water, based on the total weight of the granulate. |

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12. A liquid formulation comprising a composition according to claims 1 – 9.
13. A detergent formulation comprising
- 5 I) from 5 to 70 wt-% A) of at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing agent formulation,
- II) from 5 to 60 wt-% C) of at least one builder substance, based on the total weight of the washing agent formulation,
- 10 III) from 0 to 30 wt-% D) of at least one peroxide and, optionally, at least one activator, based on the total weight of the washing agent formulation, and
- IV) from 0.001 to 1 wt-% E) of at least one granulate which contains
- 15 a) from 2 to 75 wt-% of at least one water-soluble phthalocyanine compound and at least one azo dyestuff and/or at least one triphenylmethane dyestuff as defined in claim 1 - 9, based on the total weight of the granulate,
- b) from 10 to 95 wt-% of at least one further additive, based on the total weight of the granulate, and
- c) from 0 to 15 wt-% water, based on the total weight of the granulate,
- 20 V) from 0 to 60 wt-% F) of at least one further additive, and
- VI) from 0 to 5 wt-% G) water.
14. A softener composition comprising
- 25 (a) a composition comprising at least one photocatalyst and at least one azo dyestuff and/or at least one triphenylmethane dyestuff, as defined in claims 1 - 9, and
- (b) a fabric softener.
15. A shading process using a composition as claimed in claims 1 – 14.
- 30 16. Textile treated with a composition as claimed in claims 1 - 14.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP2004/051627

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/40 C11D17/06 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 03/018738 A (UNILEVER PLC; LEVER HINDUSTAN LTD; UNILEVER NV) 6 March 2003 (2003-03-06) example 3	1-5, 9-11, 13-16
A	US 3 762 859 A (TRIMMER R ET AL) 2 October 1973 (1973-10-02) example 1	1-3,6,7, 9-16
A	US 6 291 412 B1 (KVITA PETR ET AL) 18 September 2001 (2001-09-18) claim 7	1-5,9-16
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

7 September 2004

Date of mailing of the international search report

15/09/2004

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Saunders, T

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/051627

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

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International Application No

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